

FEATURE ARTICLE

Structure–Property Relationships in Third-Order Nonlinear Optical Chromophores

Rik R. Tykwinski,^{*,†} Ulrich Gubler,[‡] Rainer E. Martin,[§] François Diederich,^{*,§}
Christian Bosshard,^{*,‡} and Peter Günter[‡]

Department of Chemistry, University of Alberta, Edmonton, Alberta, T6G 2G2 Canada, Laboratorium für Organische Chemie, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich, Switzerland, and Nonlinear Optics Laboratory, Institute of Quantum Electronics, ETH-Hönggerberg, CH-8093 Zürich, Switzerland

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Scientists have sought for over two decades to incorporate the necessary attributes of transparency, stability, and high nonlinear susceptibilities into optimized organic or organometallic chromophores for third-order nonlinear optical (NLO) applications. These investigations have provided an ever-expanding understanding of structure–function relationships for the second hyperpolarizability γ and the bulk third-order nonlinear optical susceptibility $\chi^{(3)}$ in organic materials, which are reviewed herein. Contributing to this understanding are the studies of the third-order NLO properties displayed by an array of structurally related organic chromophores based on the conjugated carbon skeletons of hex-3-ene-1,5-diynes (1,2-diethynylethenes, DEEs) and 3,4-diethynylhex-3-ene-1,5-diynes (tetraethynylethenes, TEEs). A comprehensive series of donor (D) and/or acceptor (A) substituted derivatives of DEEs and TEEs has been measured by third-harmonic generation (THG) experiments, and the investigations on these one- and two-dimensionally conjugated chromophores have provided fundamental insight into routes leading to enhanced optical nonlinearities. The molecular characteristics identified to impact the second hyperpolarizability γ include conjugation length, heteroaromatic conjugation, degree of D/A substitution, *cis*, *trans*, and *geminal* D/A conjugation, and molecular asymmetry. A comparison of NLO properties for small molecular systems to those of a number of larger oligomers based on the DEE and TEE framework is also presented.

1. Introduction

Nonlinear optical (NLO) materials and their unique properties have sparked the imagination of chemists and physicists alike, as they make possible a wide range of processes and applications that will almost certainly be prerequisite to the realization of all-optical computing and signal processing. Since its inception over 30 years ago, the field of nonlinear optics has experienced periods of rapid development as well as encountered numerous obstacles as scientists struggled to master the propagation of light. Many milestones have thus been attained, and this progress has afforded numerous useful applications of NLO effects such as frequency doubling, frequency tripling, and parametric fluorescence, which are now common technology in today's research laser instrumentation. Owing predominately to a lack of suitable materials, however, practical applications utilizing other NLO processes have been much less developed. This is particularly true of third-order NLO phenomena such as the optical intensity dependence of refractive indices, which provides the basis of all-optical information processing.

To date, applications exploiting the nonlinear optical properties of materials have relied almost exclusively on ferroelectric inorganic crystals such as potassium dideuterium phosphate

(KD₂PO₄, KDP), lithium niobate (LiNbO₃), potassium niobate (KNbO₃), or β -barium borate (BaB₂O₄, BBO), despite shortcomings such as difficulties in materials processing. During the past two decades, interest in organic and organometallic compounds for both second and third-order NLO applications has been steadily increasing.^{1–11} These materials offer numerous distinct advantages over their inorganic counterparts, including comparable or greater off-resonance susceptibilities, fast nonlinear response times, and lower costs. The most attractive characteristic of organic based materials, however, derives from the versatility of modern organic synthetic methods, which enable the chemist to tune the photophysical properties of a material to enhance a particular NLO effect simply by altering its chemical structure. In addition, flexible synthetic routes also allow incorporation of functional groups for solubility, which greatly facilitates processing of polymers into devices and further enhances their appeal.

The induced polarization p of any molecule can be expanded in a power series of the driving electric field E with α being the linear polarizability and β and γ the first and second hyperpolarizabilities, respectively.

$$p_i = \epsilon_0(\alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l + \dots) \quad (1)$$

Summation over common indices is assumed. In bulk samples, the polarization per volume is considered, leading to the susceptibility χ and nonlinear susceptibilities $\chi^{(2)}$ and $\chi^{(3)}$.

[†] University of Alberta. Fax: 403 492 8231. E-mail: rik.tykwinski@ualberta.ca.

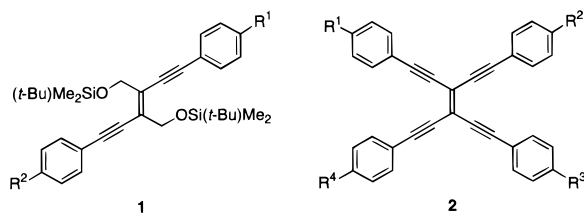
[‡] Institute of Quantum Electronics. E-mail: bosshard@iqe.phys.ethz.ch.

[§] Laboratorium für Organische Chemie. Fax: +41 1 632 1109. E-mail: diderich@org.chem.ethz.ch.

Prior to engaging in a survey of structure–function relationships for organic third-order NLO materials, it should be pointed out that one must be extremely cautious when attempting direct comparisons of hyperpolarizabilities γ (and to a lesser extent the bulk nonlinear susceptibility $\chi^{(3)}$) derived from experiments using different techniques or when comparing experimental and theoretical results.¹² There are any number of pitfalls that must be considered, including among others: (i) local field effects resulting from gas-, solution-, or solid-phase environments, (ii) a need for consistent choice of conventions in defining the nonlinearities, (iii) resonantly enhanced values, and (iv) dispersion effects resulting from measurements conducted at varying fundamental frequencies. This having been said, however, it is many times true that only the relative values of the hyperpolarizabilities are important for making comparisons, provided the quantities being compared have been measured with the same technique. In these cases, structure-dependent trends can be accurately identified and absolute values become less important.

Conjugated organic and organometallic compounds have great potential as new third-order NLO materials as a result of their highly polarizable π -electron systems. Despite the considerable efforts of both chemists and physicists, however, there is currently no one candidate that is able to fulfill all the requirements necessary for practical application and device fabrication, criteria which include transparency, stability, high nonlinear susceptibilities, and processability.^{13,14} For many years, optimization of the second hyperpolarizability γ and the bulk third-order nonlinear optical susceptibility $\chi^{(3)}$ has been pursued using conjugated, semiconducting organic polymers. As the nonlinear response of these materials was optimized by increasing their conjugation length, however, practical applications have been plagued by their low-energy optical absorptions and a general lack of thermal and environmental stabilities. Therefore, alternative materials needed to be designed and realized, and recent intents have sought to optimize third-order materials by exploiting structural characteristics other than increased conjugation length to enhance optical nonlinearities.

The interdisciplinary efforts of our groups during the last several years have targeted an understanding of structure–function relationships for the second hyperpolarizability γ and the third-order nonlinear optical susceptibility $\chi^{(3)}$ by studying donor (D) and/or acceptor (A) substituted derivatives of 1,2-diethynylethenes (DEEs, hex-3-ene-1,5-dienes, **1**) and tetraethynylethenes (TEEs, 3,4-diethynylhex-3-ene-1,5-dienes, **2**), two novel classes of one- and two-dimensionally conjugated third-order NLO chromophores, respectively. In addition to their unique structures with fully planar carbon skeletons, these compounds are synthetically accessible via short, high-yielding procedures, and they are thermally stable and unaffected by air or moisture under typical laboratory conditions.^{15–21}



In contrast to chromophores with similar structures such as *cis*-stilbenes or tetraphenylethenes, the expanded, conjugated frameworks of DEEs and TEEs preclude unfavorable steric interactions between pendant functionality. Thus, aryl rings with donor and/or acceptor (D/A) functionality attached to the central

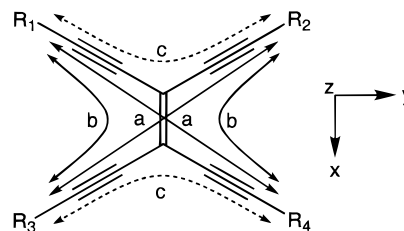


Figure 1. Conjugation paths and molecular coordinate system for a tetraethynylethene (TEE) molecule. Paths a and b afford *trans* and *cis* linear conjugation between pendant substituents, respectively, whereas path c affords cross-conjugation.

enediynes core achieve coplanarity, and, for all chromophores, electronic effects can be isolated from steric effects. For tetrakis-arylated TEE derivatives such as that illustrated in Figure 1, the two-dimensional framework allows six possible conjugation paths between the pendant functional groups, four via linear conjugation (paths a and b) and two via cross-conjugation (paths c).

We have explored the NLO behavior of a diverse range of DEE and TEE derivatives with and without pendant D/A substituents by third-harmonic generation (THG) measurements,^{19,22–25} and this feature article discusses the most significant findings from these studies. We demonstrate that the degree and pattern of D/A substitution around the central core have profound and fundamental effects on the second hyperpolarizability γ , which can be exploited to afford stable, potentially useful NLO materials. Furthermore, the dependence of γ from additional variables such as conjugation length, donor strength, heteroaromatic conjugation, lowest energy electronic absorption maximum (λ_{max}), and molecular asymmetry will be highlighted. In addition, the scope of our investigations has been further extended by incorporating selected DEE and TEE derivatives as monomeric components into oligomers and polymers.^{19,23,25} In investigations of these multianometer-sized systems, we strive to extend our understanding of structure–function relationships to larger molecules based on the conjugated DEE and TEE frameworks, ultimately targeting materials with optical nonlinearities and stabilities suitable for device fabrication.

As a prelude to discussing the data for DEE and TEE chromophores, work by other groups will be reviewed in the Background section. This survey by no means includes all of the organic and organometallic materials that have been reported. It concentrates, however, on investigations that have attempted to correlate molecular and electronic structure with observed NLO behavior. As will be seen, systematic studies of numerous polymers, oligomers, and molecules have indeed successfully identified many structural guidelines toward optimizing molecular hyperpolarizabilities γ and bulk susceptibilities $\chi^{(3)}$. At the same time, many of these studies have also shown that linearly conjugated compounds such as polyenes or polythiophenes—systems frequently considered for third-order nonlinear optics—will likely fail to meet all the necessary requirements for practical applications as a result of instabilities or saturation effects. This fact has resulted in the more recent investigation of γ and $\chi^{(3)}$ for molecules with less traditional molecular architectures. In particular, our work and that of others have shown that molecules incorporating two-dimensional conjugation and low molecular symmetry appear among the most promising candidates for optimized third-order NLO materials.

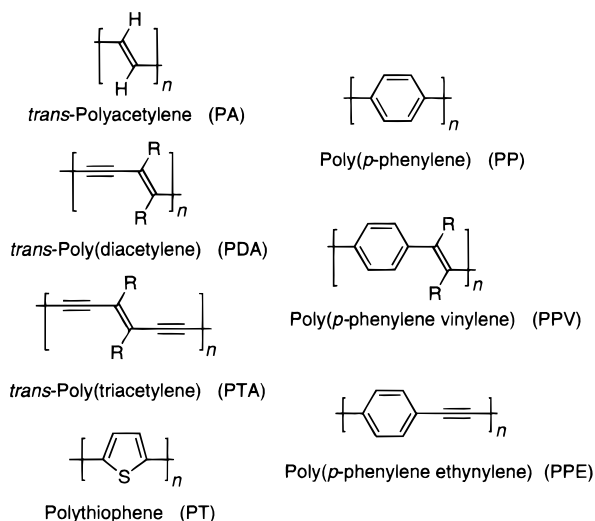


Figure 2. Structures of polymers commonly investigated for third-order optical nonlinearities.

2. Background

A. Organic Materials. Despite a wide range of reported studies, current knowledge of the structure property relationships that dominate the second hyperpolarizability γ and the bulk third-order nonlinear optical susceptibility $\chi^{(3)}$ remains rather vague, particularly in comparison to the first hyperpolarizability β and the second-order nonlinear optical susceptibility $\chi^{(2)}$.^{4,8,26} Experimental investigations during the last two decades or so have, however, identified a number of important trends.

The third-order NLO properties of numerous alkanes received early attention,^{27,28} and reports have continued to appear for these and other saturated systems.^{29–32} It was quickly realized in the study of organic third-order NLO materials that extended π -electron delocalization could be used to significantly enhance γ and $\chi^{(3)}$ values. Thus, the majority of attempts to optimize γ and $\chi^{(3)}$ have focused on the use of conjugated organic compounds, and materials such as polyacetylenes (PAs, and other polyenes),^{27,33} poly(diacetylene)s (PDAs),^{34,35} and polythiophenes (PTs)^{36,37} have been ardently investigated (Figure 2).

The relationships between γ -values and conjugation length for numerous specific organic systems have been studied both theoretically and experimentally, and it has been established that γ can generally be related exponentially to conjugation length (number of repeat units), N , in the form $\gamma \propto N^n$. Theoretical predictions have usually afforded exponents, n , in a range from 3 to 5.4.^{38–45} Experimentally, exponent values are dependent upon both substitution and structure. For example, a series of solubilized polyenes arrived at via ring-opening metathesis and studied by electric field induced second harmonic generation (EFISH) showed that γ varied with $n = 3.6$. Using the three-level model to extrapolate values to zero frequency, $\gamma(0)$, showed $n = 3.2$ for the same series.⁴⁶ Unfunctionalized PA showed $n \approx 2.5$, and γ reached a saturation level at about $N = 120$ double bonds, an N value much larger than had been predicted by theory.⁴⁷ Substituted PAs gave exponents in the range of $n = 2.3$ – 4.6 , contingent upon the pendant substituents and clearly highlighting the relationship between the electronic characteristics of the conjugated backbone and third-order susceptibilities.^{6,48}

The relationship between conjugation length and the vibrational second hyperpolarizability has been studied for oligo(*p*-phenylene)s, oligorylenes (Figure 3), and oligoacenes.⁴⁹ The

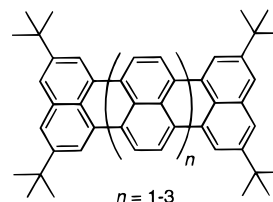


Figure 3. Chemical structure of perylene oligomers named oligoarylenes.⁴⁹

oligoarylenes were found to show the largest γ -values and afforded a steep power law relationship with $n = 5.6$. Relationships between γ and the number of π -electrons have also been derived and interpreted for these systems, as have scaling laws for comparison of γ or $\chi^{(3)}$ to the lowest energy electronic absorption maximum (λ_{max}).^{49,50}

Early studies of polythiophene (Figure 2) oligomer thin films by THG showed that $\chi^{(3)}$ values steadily increased as a function of oligomeric length and revealed that spatial conformation of the molecules also had a significant influence.⁵¹ The study of polythiophene oligomers (mono- through hexamer) via degenerate four-wave mixing (DFWM) experiments gave a power law fit with $n = 4$,⁴³ whereas later studies of polythiophene oligomers by THG gave $n = 2.8$.⁵² Saturation of the second hyperpolarizability γ for alkyl-substituted oligothiophenes was reported by Thienpont et al. to occur at about the heptamer,⁵³ but Cheng et al. have suggested that this saturation may be due to resonance effects.⁵² For bulk nonlinear optical susceptibilities $\chi^{(3)}$ of polythiophenes, the THG measurements of alkyl-substituted polythiophene thin films showed strong evidence for saturation of $\chi^{(3)}$ and predicted that $\chi^{(3)} = 1 \times 10^{-10}$ esu would be the upper limit for unsubstituted, fully conjugated polythiophene polymers.^{54,55} The outlook for improving $\chi^{(3)}$ of substituted polythiophenes appears better. Recently reported polymers constructed of an alternating pattern of substituted thiophenes and unsubstituted bithiophenes have shown enhanced $\chi^{(3)}$ values as high as 10^{-8} esu as measured by DFWM.⁵⁶ Insertion of ethynediyl ($\text{--C}\equiv\text{C--}$) units between the individual thiophene moieties gave $n = 2.4$ for poly(3-ethylthienylene ethynylene)s, and this system saw saturation of γ at about 10 monomer units (30 double and triple bonds).⁵⁷ Values of γ for oligo(thienylene vinylene) and oligo(thienylene ethynylene) systems with 2–5 thiophene units have been measured, but resonant effects hampered interpretation of these results.⁵⁸ A direct comparison of poly(arylene ethynylenes) with the arylene moieties being thienyl rings, phenyl rings, or both showed that $\chi^{(3)}$ could be substantially enhanced as a direct result of the increased π -electron delocalization caused by charge-transfer (CT) interactions between the alkyne (electron acceptor) and aryl ring (electron donor) in these systems.^{59,60}

The nature of effective conjugation length was examined by DFWM for γ in a series of poly(*p*-phenylene)s in comparison to polythiophene oligomers of equal length and showed that the onset of γ saturation occurs in poly(*p*-phenylene)s at a shorter length than in polythiophenes.⁶¹ This same study also systematically considered the effects of functionalized α -terthiophene (α -terthienyl, a PT trimer) derivatives and revealed that (i) substitution of a pyrrole or benzene unit in place of the central thiophene ring reduced γ -values, (ii) substitution of iodine atoms at the terminal α -positions (α to the S-atom) increased γ , and (iii) large increases in γ could be gained from mono or dinitro substitution at the terminal α -positions of terthiophenes.

The magnitude of γ has been determined by THG for members of a series of α,ω -diphenylpolyenes in studies that

probed the effects of conjugation length, end group substitution patterns, and the use of alkoxy groups as solubilizing substituents.^{62,63} The steepest increases in γ were measured for asymmetric donor–acceptor (D–A) substituted polyene derivatives. Quite surprisingly, however, this study also found that centrosymmetric bis-acceptor derivatives (bis-nitrophenyl) had much larger γ -values than bis-donor derivatives of equal length.⁶² Conversely, other reports have suggested a predominant role for donor substituents for increasing γ -values. For example, studies of poly(*p*-phenylene ethynylene) oligomers have shown the importance of electron donor (alkoxy) groups toward optimizing γ for these materials.^{64,65} THG measurements of nitrogen containing polyenes, polyazines, end-capped with electron-donating amino groups also showed significant gains in γ as a function of oligomeric length, and a rather steep power law relationship with $n \approx 3$.^{14,66}

With a molecular structure similar to polyenes, cyanine dyes have been investigated for their NLO behavior as a function of both substitution and conjugation length.^{67–70} Increases in γ versus the number of π -electrons in these symmetrically end-capped molecules ultimately depends on end group substitution. To date, the thiacyanines exhibit sharpest gains versus conjugation length—a trend that unfortunately ends with saturation of γ at ca. 1×10^{-33} esu.⁶⁷

As a comparison to polyene oligomers, end-capped polyyne oligomers have also been investigated by THG measurements, considering both the nature of the end-capping group as well as the number of conjugated triple bonds between these groups.⁷¹ As the number of triple bonds was increased in trialkylsilyl end-capped derivatives, $\chi^{(3)}$ increased significantly and did not scale simply according to the expected power law relationship based on conjugated repeat units. This suggested an additional contribution from the mildly electron-donating silyl moiety. Replacement of the silyl groups by ferrocenyl groups in a buta-1,3-diyne derivative produced a substantial $\chi^{(3)}$, as did replacement of the butadiyne moiety by a buta-1,3-diene fragment. This comparison ultimately hinted at better proficiency for alkene vs alkyne linkers between the end-capping groups to increase polarization in these conjugated molecules.

Marder and co-workers elegantly related the magnitude of the second hyperpolarizability γ to the extent of bond length alternation (BLA) in D–A substituted polyenes, specifically polymethine dyes, using both experimental and theoretical results.^{72–76} By tuning the BLA via chromophoric structure, solvation effects, or an external electric field, γ could be optimized in either a positive or negative sense for polymethine dyes of a given length. These same studies, and others,⁷⁷ suggested a strong correlation between linear and nonlinear optical properties (α , β , γ) of conjugated organic molecules and successfully allowed for prediction of NLO properties based on molecular structure. Interestingly, these studies also predicted that as the first hyperpolarizability β is maximized for a given chromophore, the second hyperpolarizability γ should approach zero, suggesting a limit to the ability of D–A substitution to increase γ -values.

Benzene derivatives, stilbenes, and related aromatic structures have been systematically modified toward enhancing γ -values by introducing a large variety of donor and/or acceptor functional groups. In the mid-70s, Oudar and co-workers had already derived a number of trends for γ based on four-wave mixing experiments of benzene and stilbene derivatives.^{78–80} These early studies showed, for example, (i) a greater than 2-fold increase in γ for *trans*-stilbene in comparison to *cis*-stilbene, (ii) a strong correlation between γ -values and the mesomeric

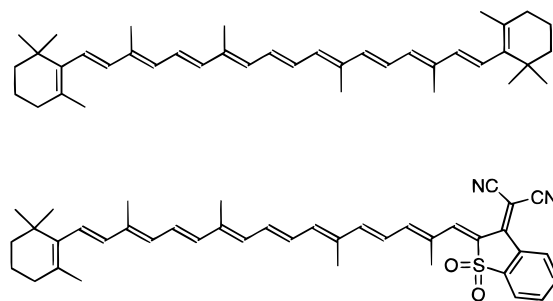


Figure 4. Chemical structure of naturally occurring β -carotene ($\gamma = 1 \times 10^{-32}$ esu, top) and carotenoid derivative reported by Marder et al.⁸³ with a very large second hyperpolarizability of $\gamma = 35 \times 10^{-32}$ esu (bottom).

effects of the substituents, and (iii) the influence of intramolecular charge transfer (CT) on γ -values. A comprehensive study was later reported by Cheng and co-workers who conducted THG measurements for a wide range of asymmetrically substituted donor–acceptor π -electron systems.^{63,81} These two reports included results for functionalized benzenes, stilbenes, styrenes, biphenyls, fluorenes, diphenylacetylenes, various phenylvinyl heterocycles, oligomeric polyphenyls, α,ω -diphenylpolyynes, α -phenylpolyenes, α,ω -diphenylpolyenes, and other extended phenylvinyl derivatives. From this large data set, trends toward optimizing γ as a function of the nature of the conjugated linkers between the aromatic moieties, molecular geometry, aromaticity and bond length alternation, electron delocalization effects, conjugation length, and the electronic biasing effects of various donors and acceptors could be evaluated. Salient features determined were (i) a general dependence of γ on conjugation length, (ii) higher γ -values for electron-deficient benzene and monosubstituted stilbene derivatives, and (iii) a strong correlation between γ and β and the longest wavelength absorption maximum (λ_{\max}) that further established a link between γ and the CT nature of these one-dimensional chromophores.

The naturally occurring carotenoids and similarly structured polyenes have been favorite targets for elucidating third-order NLO trends (Figure 4).^{27,82–89} Early analysis of this class of compounds found γ to increase superlinearly with increasing conjugation length.²⁷ Investigations of symmetric bis-donor or bis-acceptor and asymmetric donor–acceptor push–pull derivatives showed that lengthening the polyene chain resulted in sharp increases in γ . Very large values (γ up to $56\,600 \times 10^{-36}$ esu) were measured for long push–pull carotenoids,⁸⁷ and symmetric carotenoids with donor end groups displayed the steepest increases in γ as function of conjugation length.⁸⁴ The exponential relationship $\gamma \propto N^n$, where N is the number of double bonds, could be modeled for these polyenes, and the exponent n was found to be dependent upon both the electronic characteristics of the end groups and the substitution pattern (i.e., D–D, A–A, or D–A). No saturation of γ has so far been observed within the size range of carotenoid molecules investigated, which extend to lengths up to 4 nm.^{84,86,87} Investigations within a series of carotenoids of comparable length but increasing intramolecular charge transfer interactions recently showed that the increase in polarization within these molecules produced a 35-fold increase in γ relative to the symmetric molecule β -carotene at the lowest energy absorption maximum λ_{\max} (Figure 4).⁸³ Carotenoids have also been utilized to probe dispersion⁸⁵ via comparison of experimental results to the three-level model.⁹⁰

The third-order NLO properties of a series of model compounds constructed from benzothiazole, benzimidazole, and

benzoxazole cores have been investigated by DFWM.^{91,92} Structure–property relationships determined for these molecules include the following: (i) the second hyperpolarizability γ increases rapidly with increased conjugation length for quasi-one-dimensional molecules, (ii) the incorporation of heteroatoms into the π -electron system can be beneficial to γ , (iii) the incorporation of heteroaromatic conjugation units containing sulfur atoms enhances nonlinearities as do (iv) electron-donating alkoxy substituents on aromatic rings, and (v) π -electron delocalization in two dimensions enhances γ without reducing optical transparency.

DFWM studies of tetrasubstituted cumulenenic compounds have shown that these conjugated chromophores with two mutually perpendicular π -electron systems possess high polarizabilities and are relatively efficient NLO chromophores.^{93,94} There were, however, significant problems with resonant enhancement of the values. Nonetheless, two trends emerged: (i) aryl substituents make a substantial contribution to the conjugation length, and thus γ , and (ii) somewhat surprisingly, there is little enhancement of γ resulting from electron donor or donor–acceptor functionalization on the cumulenenic framework.

Squarylium dyes have been shown by EFISH,^{95,96} THG,⁹⁶ DFWM,⁹⁷ Sagnac pump–probe measurement,^{95,98} and the quadratic electrooptic effect^{95,99,100} to possess substantial optical nonlinearities, with γ -values up to an order of magnitude higher than those measured for benzenoid aromatic molecules of comparable size. Off-resonant EFISH measurements have firmly established that the third-order optical nonlinearity of squarylium dyes is negative, which is relatively uncommon among organic chromophores.⁹⁶ The structural and theoretical origins of this negative third-order polarizability have subsequently received considerable attention, with the role of two-photon contributions to the second hyperpolarizability γ at the center of these studies.^{95,96,101–104}

Numerous other organic materials have been evaluated as third-order NLO chromophores as a function of their structural features. These systems include intermolecular charge-transfer complexes,^{105–107} phenylethynyl-substituted benzene systems,¹⁰⁸ tetrathiafulvalene derivatives,¹⁰⁹ polyradicals,¹¹⁰ and the fullerenes.¹¹¹

B. Organometallic Materials. The incorporation of transition metal centers into a conjugated organic system provides yet another dimension in NLO chromophore design, and organometallic systems have been well-studied for third-order NLO applications.^{112,113} These investigations provide additional guidelines for optimized chromophores based on factors such as the ability of the metal center to act as an electron donor and/or acceptor, as well as the ability of the metal center to contribute to π -electron conjugation. Metal participation in π -electron delocalization in organometallic complexes via interaction of transition metal d-orbitals with the conjugated π -orbitals of the organic moiety has indeed been shown to enhance optical nonlinearities.¹¹² Furthermore, additional control and manipulation of the photophysical properties of chromophores has been achieved by varying both the ligands attached to the metal centers as well as their oxidation state.

Metallocenes have been widely examined, including hafnocenes, ruthenocenes, zirconocenes, and titanocenes,¹¹⁴ as well as numerous lanthanide derivatives.¹¹⁵ It was concluded that the γ -values of organometallic derivatives were generally comparable to their organic counterparts of similar structure, and in many cases substantial enhancements in the second hyperpolarizability γ were measured. The second hyperpolarizabilities determined for group 4 (Ti, Zr, Hf) metallocene

σ -acetylide complexes are clearly higher than the sum of the γ -values measured for the free organic alkyne and metallocene components.¹¹⁶ Comparison of the acetylide complexes to structurally similar complexes with only vinylic ligands suggested that the origin of the optical nonlinearity derives from the π -electron conjugation system, which can involve the Cp–metal (Cp = cyclopentadienyl) bonding network and suitably symmetric orbitals of the vinyl and acetylide ligands. This trend has also been observed for other organometallic systems. For example, γ for a bis(*N*-(4-nitrophenyl)thiocarbimato)Ni(II) complex exceeds by 2 orders of magnitude the γ -value arising from simple addition of the individual values of the free thiocarbimato ligands.¹¹⁷

A particularly large number of ferrocene derivatives have been studied,^{118–121} and these data provided several specific trends: (i) a rapid increase in γ -values from lengthened conjugation that ultimately reaches saturation, (ii) little contribution from the ferrocenyl group to the overall conjugation length, (iii) the π -electron delocalization through the ferrocenyl group is relatively inefficient, and (iv) increased nonlinear responses derive more from d– π^* and π – π^* transitions involving the ferrocene, whereas the d–d transitions of the metal center appear to play a much smaller role.

A number of recent investigations by Humphrey and co-workers have targeted optimization of γ in organometallic chromophores through changes in the pendant functionality of metal σ -acetylide complexes.^{122,123} Studies of ruthenium σ -acetylide complexes showed that a number of factors contributed to heightened third-order responses in these systems including: (i) the presence of an electron-accepting acetylide incorporating a NO₂ moiety, (ii) phosphine ligand substitution, and (iii) extended π -electron conjugation.¹²³ It was also postulated for these systems that increasing the conjugation length of a chromophore by addition of alkene residues is more effective for enhancing second hyperpolarizabilities than by addition of aryl or alkynyl moieties.

Other recent efforts have afforded gold σ -acetylide complexes with the largest known nonlinearities for a monomeric organometallic compound; in these complexes, the presence of the metal atom center coordinated to the alkynyl ligand is critical for the NLO response.¹²⁴ A series of ruthenium(II) complexes with coordinated para-substituted benzonitriles has been studied by THG, and it has been proposed that increased γ -values in these molecules are a result of π -electron back-donation which enlarges the overall electronic π -systems.¹²⁵ Alternatively, investigations of thin films of platinum complexes have highlighted the importance of molecular stacking arrangements in third-order NLO optimization.¹²⁶

Group 10 metals (Ni, Pd, Pt) have been incorporated into a range of σ -acetylenic frameworks to provide conjugated oligomers and polymers.^{127–131} In many cases, the presence of the metal center led to a considerable enhancement in second hyperpolarizability γ as compared to the corresponding nonligated organic components. The diverse range of metal–acetylenic complexes studied has provided a good comparison of the relative importance of the type of metal, the nature of the coordinated alkyne residue, and the overall length of π -electron conjugation.^{127–130}

Bjørnholm and co-workers examined by THG a new class of organometallic third-order NLO chromophores comprised of molecules with significant ligand to metal or other “periphery-to-center” charge-transfer transitions.^{117,132,133} Structurally, these complexes are related to the well-known triarylmethyl cations.¹³² These two-dimensionally conjugated materials exhibit multiple,

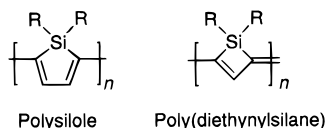


Figure 5. Structures of polysilole and poly(diethynylsilane) polymers.

intramolecular charge transfers from the peripheral functionality to the central atom which take place upon electronic excitation. These efforts have afforded one of the highest, albeit resonantly enhanced, reported γ -values (3×10^{-32} esu) for an organometallic complex.¹³³

C. Theoretical Studies. The number of theoretical studies aimed at optimizing third-order NLO behavior has been rapidly expanding in the past several years.^{2,134} In addition to investigating traditional conjugated molecules and polymers, reports now include a variety of structural features and variations not previously considered, such as spiroconjugation,¹³⁵ which could offer the advantages of both increased transparency as well as substantial γ and $\chi^{(3)}$ values. A theoretical study has elaborated on the well-known correlation between conjugation length and γ to include curved aromatic molecules by considering surface area rather than length.¹³⁶ These relationships provide a useful means of comparing aromatic hydrocarbons of widely differing structure and interpreting how curvature influences γ . Unsubstituted, planar, polycyclic aromatic hydrocarbons have also been considered, and the relationship between second hyperpolarizability γ , resonance energy, and topology have been determined.¹³⁷ The effects of aromatic and heteroaromatic conjugation have recently been outlined,¹³⁸ as have the effects of the π -bonding sequence in chromophores using π -bridges composed of carbon and/or nitrogen.¹³⁹ Nontraditional, π -conjugated polymer backbones have been studied theoretically, and large optical nonlinearities have been projected for polymers composed of polysilole,¹⁴⁰ in comparison to the known poly(diethynylsilane) polymer (Figure 5).¹⁴¹ Unfortunately, the limited space of this feature article allows only this very brief description of current theoretical studies of third-order NLO materials which bear increasing predictive power.^{2,134}

3. Experimental Considerations

A. Synthesis of DEE and TEE Derivatives. The synthesis of molecules **3b–f**,¹⁹ **5**, **7–8**, **11**, and **13–31**,^{20,21} **6** and **9**,¹⁶ **32–37**,¹⁵ **41** and **44–46**,²³ **3a** and **42–43**,²⁵ **40a**,¹⁴² and **40b–c**,¹⁴³ have been reported. All new compounds were fully characterized by ¹H and ¹³C NMR, IR, UV/VIS, MS and by combustion analysis or high-resolution mass spectroscopy. More than 10 X-ray crystal structures demonstrate the planarity of the DEE and TEE cores including, in most cases, the appended substituted phenyl rings.^{15,19–21,142,143}

B. NLO Methods. In the present case, the third-order optical nonlinearities have been studied by third-harmonic generation (THG) in chloroform solutions. In an isotropic liquid, only the rotational average second hyperpolarizability γ , of γ_{ijkl} needs to be considered (eq 2).

$$\gamma = \frac{1}{5}(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + \gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz} + \gamma_{yyxx} + \gamma_{zzxx} + \gamma_{zzyy}) \quad (2)$$

$$\chi^{(3)}(C) = N_A \frac{d(C)f(C)}{1+C} \left(\frac{\gamma_s}{M_s} + C \frac{\gamma_m}{M_m} \right) \quad (3)$$

Experimentally, the macroscopic third-order nonlinear optical susceptibility $\chi^{(3)}(-3\omega, \omega, \omega, \omega)$ of the solutions has been

measured. It is related to the molecular averaged γ by eq 3,¹⁴⁴ where C is the concentration, expressed as the ratio of the total weight of the solute molecules to the weight of the solvent, N_A is Avogadro's number, $d(C)$ is the density of the solution, and $f(C)$ is the local field correction factor in the Lorentz approximation using the refractive index of the solvent.¹⁴⁵ M_s and M_m are the molecular masses of the solvent and the solute, respectively. The densities of the measured solution were taken to be that of the solvent, CHCl₃, and assumed to be constant over the range of dilutions measured.

In eq 3, it is assumed that $\chi^{(3)}$ depends linearly on the sample concentration for small concentrations. From the determined second hyperpolarizability γ , a bulk value $\chi^{(3)}_{100\%}$ for a pure molecular sample was estimated by assuming an isotropic arrangement of the molecules and using the density and refractive index of the solvent, CHCl₃. An optimized orientation of the molecules in a crystalline state or thin film should afford even larger values of $\chi^{(3)}_{100\%}$. A more realistic refractive index of ca. 1.7 for the solid chromophores would afford values of $\chi^{(3)}_{100\%}$ that could be twice as large. Whereas the $\chi^{(3)}_{100\%}$ values are less useful in evaluating the effects of structural changes on the hyperpolarizabilities, they nonetheless offer an approximation of the macroscopic nonlinearity per unit volume and are useful for comparison to other chromophores and oligomeric derivatives. No attempt was made to calculate γ -values extrapolated to zero frequency since no accurate description of the dispersion of the nonlinearity in these molecules currently exists.

C. Third-Harmonic Generation. For third-harmonic generation experiments, chloroform solutions of the chromophore in concentrations between 0.1 and 4 wt % were measured in a 1 or 0.2 mm thick fused silica cuvette. For measurements at 1.907 μ m, a pulsed Nd:YAG laser ($\lambda = 1.064 \mu$ m, 10 Hz, 5 ns) pumped a H₂-Raman cell yielding a frequency-shifted wavelength of 1.907 μ m. Measurements at 2.1 μ m utilized a pulsed HoTmCr:YAG laser (2 Hz, 80 ns).^{22,23} The experimental setup included a splitting of the incident beam to generate a reference signal that could be used to correct against power fluctuations and drift at the fundamental frequency.

At both fundamental wavelengths, the s-polarized beam was focused onto a cuvette with a $f = 500$ mm lens. Third-harmonic generation measurements were performed by rotating the sample parallel to the polarization to generate Maker-fringe interference patterns, which were analyzed in a manner similar to that previously described.³¹ All measurements were calibrated against fused silica $\chi^{(3)} = 3.9 \times 10^{-22}$ m² V⁻² ($= 2.8 \times 10^{-14}$ esu).¹⁴⁶ A comparison of measurements of fused silica in a vacuum and in air allowed all subsequent measurements to be performed in air. If necessary, a correction for sample absorption at the third harmonic frequency was made using absorption coefficients measured with a standard spectrometer. For each material, measurements of $\chi^{(3)}$ for pure CHCl₃ and for 2–5 different sample concentrations were done, and the second hyperpolarizability γ was obtained by a fit to eq 3. If not otherwise stated, the relative error for these measurements is approximately 10%.

4. Results and Discussion

A. Tetraethynylethenes (TEEs) vs Diethynylethenes (DEEs). The experimental THG results for functionalized DEEs **3–12** and TEEs **13–37** at 1.9 and 2.1 μ m are presented in Tables 1 and 2, respectively, as are the wavelengths of the lowest energy electronic absorption maxima (λ_{\max}) and the molar extinction coefficients (ϵ) of absorptions at the third harmonic

TABLE 1: Results of Third-Harmonic Generation Experiments at 1.9 μm

	λ_{max} [nm] ^a (ϵ) ^b	ϵ (636 nm) [mol/(cm dm ³)]	γ [10 ⁻³⁶ esu]	γ [10 ⁻⁴⁸ m ⁵ /V ²]	$(\chi^{(3)} 100\%)/\chi_{\text{fs}}^{(3)c}$
3a	296 ^d (19 700)	0	22	0.32	5
3b	378 ^d (24 200)	0	108	1.51	13
4	354 (23 800)	0	122	1.71	23
5	366 (35 700)	0	117	1.64	23
6	372 (45 300)	0	210	3.0	37
7	397 ^e (51 400)	0	300	4.2	54
8	424 (25 000)	0	610	8.5	108
9	368 (23 700)	0	230	3.3	41
10	395 (56 500)	0	530	7.4	58
11	416 (68 300)	0	1070	15	119
12	442 ^e (39 600)	0	1120	15.6	124
13	382 (28 200)	0	95	1.3	17
14	433 (29 300)	0	270	3.8	48
15	375 (36 200)	0	130	1.8	25
16	428 (51 100)	0	310	4.3	50
17	447 (19 900)	8	59	0.83	10
18	403 (34 000)	0	230	3.2	36
19	459 (41 000)	0	420	5.8	68
20	468 (31 200)	0	1000	14	170
21	471 (17 000)	0	1100	16	180
22	428 (28 900)	0	240	3.4	43
23	461 (38 300)	53	1500	21	260
24	486 (40 700)	430	3200	44	570
29	456 (41 600)	0	530	7.4	52
30	486 (45 100)	220	1900	27	190
31	481 (31 300)	0	3600	50	350

^a λ_{max} is the longest wavelength electronic absorption maximum as measured in CHCl_3 . ^b Molar extinction coefficient. ^c $\chi^{(3)}$ of fused silica (fs), for which a value of $\chi^{(3)} = 3.9 \times 10^{-22} \text{ m}^2/\text{V}^2$ (2.8×10^{-14} esu) has been used; see ref 146. ^d Values obtained by deconvolution of the absorption spectra; see ref 19. ^e Shoulder absorption.

frequencies (636 or 700 nm).^{19,22,24} Several fundamental conclusions were drawn from these THG data on the basis of functionality, conjugation length, substitution pattern, and molecular framework. First, chromophores with the two-dimensionally conjugated TEE framework generally display increased second hyperpolarizabilities γ in comparison to one-dimensionally conjugated DEEs (measured at 1.9 μm , Table 1). The effects of two-dimensional conjugation are less notable in acceptor functionalized derivatives, and the values measured for *p*-nitrophenyl substituted TEEs **13** and **18** are comparable to those of the analogous DEEs **4**, **6**, and **9**. Surprisingly, this

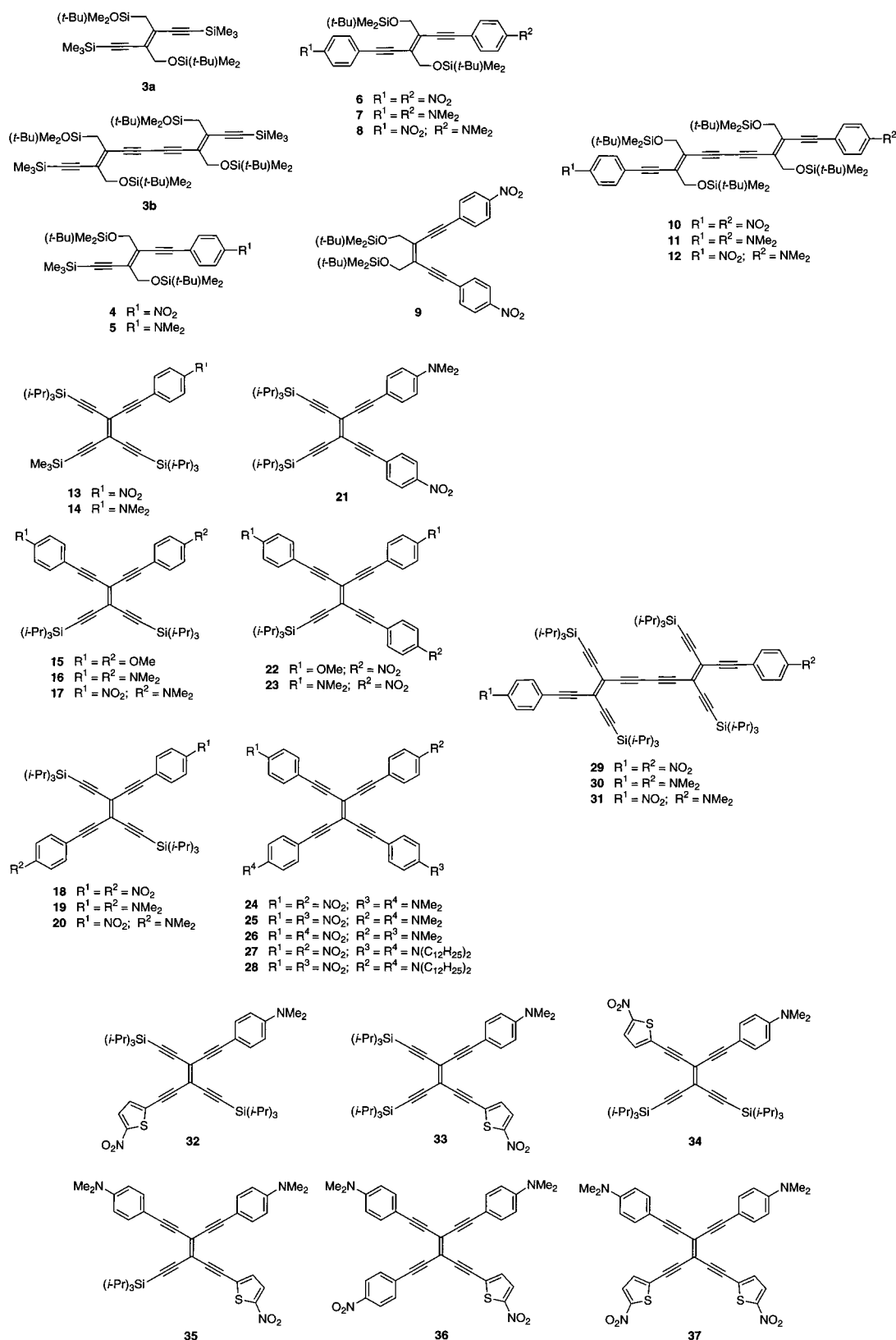
TABLE 2: Results of Third-Harmonic Generation Experiments at 2.1 μm

	λ_{max} [nm] ^a (ϵ) ^b	ϵ (700 nm) [mol/(cm dm ³)]	γ [10 ⁻³⁶ esu]	γ [10 ⁻⁴⁸ m ⁵ /V ²]	$(\chi^{(3)} 100\%)/\chi_{\text{fs}}^{(3)c}$
17	447 (19 900)	0	280 \pm 20 ^d	3.9	44
20	468 (31 200)	0	790 \pm 50	11	120
21	471 (17 000)	0	500 \pm 80 ^d	7.0	79
23	461 (38 300)	0	1110 \pm 30	15.5	190
24	486 (40 700)	90	2000 \pm 100	28	350
25	533 (22 000)	120	890 \pm 100	12	160
26	520 (23 800)	40	1590 \pm 100	22	280
27	511 (44 600)	100	2000	28	170
28	556 (24 700)	600	2300	32	200
32	477 (32 900)	0	910 \pm 30	13	140
33	500 (14 300)	10	440 \pm 20	6.2	70
34	423 (33 900)	0	380 \pm 40	5.2	59
35	477 (34 000)	70	1570 \pm 60	22	260
36	544 (33 300)	120	2550 \pm 120 ^d	36	450
37	570 (33 600)	310	2200 \pm 100	31	380

^a λ_{max} is the longest wavelength electronic absorption maximum as measured in CHCl_3 . ^b Molar extinction coefficient. ^c $\chi^{(3)}$ of fused silica (fs), for which a value of $\chi^{(3)} = 3.9 \times 10^{-22} \text{ m}^2/\text{V}^2$ (2.8×10^{-14} esu) has been used, see ref 146. ^d Represents the average of two experiments.

is also true for the extended, dimeric derivatives **10** and **29**, which show identical γ -values of 530×10^{-36} esu. In contrast, donor–donor (D–D) and donor–acceptor (D–A) substitution dramatically increases γ for TEEs versus the analogous DEEs, as can be seen by examining the γ -value of D–A-TEE **20** (1000×10^{-36} esu), which is nearly double that of D–A-DEE **8** (610×10^{-36} esu). This disparity in γ becomes more pronounced as conjugation length increases, a trend that culminates with a nearly 2-fold increase in γ for D–D-TEE **30** vs D–D-DEE **11**, and a greater than 3-fold γ enhancement measured for dimeric D–A-TEE **31** vs dimeric D–A-DEE **12**. With their additional alkyne residues, the TEE cores are better electron acceptors than DEE cores, and an increased π -electron delocalization in the D-substituted TEEs due to enhanced intramolecular charge-transfer interactions leads to increased second hyperpolarizability. Similar observations had been previously made in studies with poly(arylene ethynylene)s.^{59,60} The enhanced electron-accepting character of TEE in comparison to DEE cores had also been clearly revealed by electrochemical investigations.^{18,19}

B. Conjugation Length. A substantial increase in optical nonlinearities in both the DEE and TEE chromophore series was consistently observed upon increasing the length of the conjugated framework, irrespective of D/A substitution pattern or degree. For example, the measured second hyperpolarizabilities γ for the dimeric species DEEs **10–12** and TEEs **29–31** are 2–5 times higher than those of the corresponding monomeric DEEs **6–8** and TEEs **18–20**. These results contrast earlier findings by Cheng et al., where no enhancement of γ was observed in 4,4'-disubstituted α,ω -diphenylpolyynes upon increasing the number of triple bonds.⁶³ They are in accord,



however, with findings for functionalized polyenes, which have clearly shown that even moderate extension of conjugation length in small D–A substituted molecules can provide significant increases in γ .^{62,86} For the TEE and DEE systems described here, it should be noted that the increase in γ for dimeric chromophores **10–12** and **29–31** is concurrent with a substantial increase in molecular mass, so that there is only a

moderate gain in the macroscopic nonlinearities $\chi^{(3)}$ for the dimeric chromophores.

C. Donor Strength. Strong electron donor substituents such as *N,N*-dialkylamino groups on the appended aryl rings clearly lead to larger second hyperpolarizabilities γ than do strong electron acceptors such as nitro groups. This trend is evident in monoarylated TEEs **13–14**, *trans*-bis-arylated DEEs **6–7** and

TEEs **18–19**, as well as the dimeric species **10–11** and **29–30**. Furthermore, the strength of the electron donor is also distinctly important, as confirmed by comparison of molecules **15–16** and **22–23**, where replacement of the mildly electron-releasing methoxy substituent by the strongly donating *N,N*-dimethylamino group affords 2- and 6-fold increases in γ , respectively. Similar gains for γ as a result of increased electron density have been observed in one-dimensional systems such as stilbenes,⁸¹ polyenes,⁶² and various carotenoid systems.^{84,86,87}

The electron-donating ability of *N,N*-dialkylamino groups can be increased by exchanging *N,N*-dimethyl for *N,N*-didodecyl substitution. This increase is evidenced in the UV/vis spectra of the didodecylamino derivatives **27** and **28**, which depict substantial bathochromic shifts in λ_{max} and enhanced intramolecular charge-transfer interactions in comparison to the analogous dimethylamino derivatives **24** and **25**.²⁰ THG measurements at 2.1 μm , however, showed that the presence of the *N,N*-didodecyl groups had little impact on the second hyperpolarizability γ for **27**, which was found identical to that of the *N,N*-dimethylamino substituted **24** (2000×10^{-36} esu). The centrosymmetric D–A–TEE **28** (2300×10^{-36} esu) showed an increased γ in comparison to **25** (890×10^{-36} esu), but the stronger absorption at the third harmonic for **28** likely contributes to this increase via resonant enhancement.

D. Heteroaromatic Conjugation. Utilizing heteroaromatic thiophenes as conjugated rings in lieu of phenyl rings as a method of increasing optical nonlinearities in D/A chromophores has been explored theoretically^{147–149} and experimentally for second-order^{150–154} and, to a much smaller extent, for third-order NLO materials.^{91,92,99,155–157} Substantially increased first hyperpolarizabilities β can be realized as a result of decreased aromatic stabilization of the thiophene ring, but the effects on γ are predominantly untested.

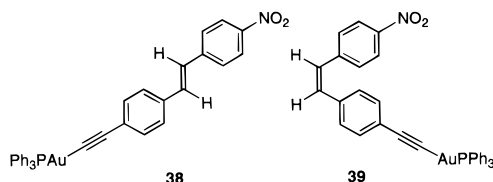
The incorporation of thiophene rings did indeed afford 1.1–1.4-fold increases in the second hyperpolarizabilities of nitrothienyl TEEs **32–37** in comparison to the analogous nitrophenyl TEEs, all measured at 2.1 μm (Table 2). The greater γ -values are, however, also accompanied by consistent red-shifts in the absorption spectra of the nitrothienyl TEEs. Thus, even when measuring THG away from resonance at 2.1 μm , it is possible that dispersion accounts for at least part of the increased γ -values that have been observed from incorporation of the heteroaromatic rings. The exception to this trend is *gem*-D–A **34**, where a 1.4-fold increase in γ is observed relative to **17**, despite a decrease in the longest wavelength absorption maximum λ_{max} for **34** (423 vs 447 nm for **34** and **17**, respectively). The unexpectedly high γ measured for tetrakis-arylated chromophore **36** where one nitrophenyl has been swapped for a nitrothienyl represents a unique case, and the increased γ seems dependent on symmetry relationships rather than aromaticity (*vide infra*).

E. Dispersion. A comparison of second hyperpolarizabilities for molecules **17**, **20**, **21**, and **23–24** measured at both 1.9 and 2.1 μm shows considerable dispersion as the third harmonic frequency moves to lower energy and farther away from resonance. This is not unexpected since, at 636 nm, the third harmonic for measurements at 1.9 μm generally falls at the very edge of the electronic absorptions of these molecules. A more detailed description of dispersion effects for TEEs, as well as extrapolation of γ to infinite wavelengths, however, is at present unattainable owing to the absence of an accurate description of the dispersion of the nonlinearity of these unique molecules.

F. Donor–Acceptor Stereochemistry. The influence of *cis*-, *trans*-, and *gem*- (geminal) substitution for bis-function-

alized TEE and DEE molecules has been considered, and several trends have emerged. Nearly identical second hyperpolarizabilities γ were measured at 1.9 μm for the A–A–DEEs *trans*-**6** and *cis*-**9**, which is not surprising in view of their equal conjugation lengths and an absence of D–A interactions. Similarly, for the D–A–TEE derivatives **20** and **21**, nearly equal γ -values have been measured at 1.9 μm although the UV/vis spectra indicated significant differences in electronic properties.²⁰ On the other hand, measurements of *trans/cis* pairs **20/21** and **32/33** at 2.1 μm both showed higher values for the *trans*-isomer than for the *cis*-isomer, as might be empirically expected on the basis of the effectiveness of the excited-state charge transfer and, thus, polarization of the molecule. The results for γ measured at 2.1 μm suggest that the values at 1.9 μm for **20/21** may be modulated by dispersion, which is subsequently alleviated for THG at the longer wavelength. A similar *trans/cis* stereochemical effect was reported for gold– σ -arylalkyne complexes (**38/39**), where γ for the *trans*-complex is about three times higher than for the *cis*-complex.¹²⁴ The γ -values for **38/39**, however, are likely influenced by steric effects, which prevent planarity in the *cis*-complex and disrupt the effective conjugation length of the molecule. This example nicely demonstrates the superiority of DEEs and TEEs over stilbenes for studying electronic effects separated from steric influences.¹⁶ Both *cis*- and *trans*-diaryl substituted DEEs and TEEs are planar, whereas *cis*-stilbenes such as **39** are distorted from planarity.

It has also been suggested that *cis*-to-*trans* isomerization in retinals is responsible for increases beyond 1 order of magnitude in nonlinear susceptibilities, but unambiguous structural proof of stereochemistry is not yet available from these experiments.¹⁵⁸



Strong contributions from stereochemical effects on γ are evident by comparison of linear conjugation (paths a and b) and cross-conjugation (paths c) between donor and acceptor substituents (Figure 1). Specifically, the presence of linear conjugation via a *trans*- or *cis*-D–A relationship is in all cases superior to a cross-conjugated, geminal D–A interaction in these chromophores. This trend is validated by γ -values at 1.9 μm for *trans*-**20**, *cis*-**21**, and *gem*-**17** (1000 , 1100 and 59×10^{-36} esu, respectively) and 2.1 μm (790 , 500 , and 280×10^{-36} esu, respectively). The nitrothienyl TEEs *trans*-**32**, *cis*-**33**, and *gem*-**34** with second hyperpolarizabilities γ measured at 2.1 μm (910 , 440 , and 380×10^{-36} esu, respectively) corroborate this trend. Effects from less efficient *gem* π -electron conjugation paths can also be observed in the comparison of *gem*-D–D–**16** to *gem*-D–A–**17**. In this case, the more electron-rich chromophore **16** shows a considerably enhanced γ -value (310×10^{-36} esu) since the two donor fragments undergo a more potent intramolecular charge-transfer interaction with the electron-accepting TEE core than the one donor fragment in D–A–TEE **17** (59×10^{-36} esu) in which, additionally, the *gem*-D–A conjugation path is not efficient. Thus, the enhancement of γ in TEEs by D–A π -electron conjugation effects can now be distinguished, decreasing in the order *trans* > *cis* >> *gem*.

G. Lowest Energy Electronic Absorption Maximum (λ_{max}). It has been observed that a bathochromic shift of the lowest energy electronic absorption maximum (λ_{max}) affords an increase in the third-order nonlinearity, an effect which has been

named as nonlinearity transparency tradeoff.⁶³ Two-dimensionally conjugated chromophores such as TEEs, however, seem to circumvent this limitation when compared to linearly conjugated molecules. For example, the second hyperpolarizability γ measured away from resonance at 2.1 μm in the series of D–A molecules **20**, **21**, **23**, and **24** shows a substantial enhancement for the two-dimensionally D–A-conjugated TEEs **23** and **24**, without a significant increase in λ_{max} . In fact, TEE **23** ($\lambda_{\text{max}} = 461$ nm) exhibits a 1.4 and 2.2-fold increase in γ (Table 2) over **20** ($\lambda_{\text{max}} = 468$ nm) and **21** ($\lambda_{\text{max}} = 471$ nm), respectively, while at the same time displaying a hypsochromic shift of the lowest energy absorption maximum. This same trend is also observed for the series of nitrothienyl derivatives **32**, **33**, and **35**. Two-dimensionally D–A conjugated **35** shows a 1.7-fold increase in γ as compared to **32**, yet the molecules have identical λ_{max} values at 477 nm. These data convincingly establish the importance of two-dimensional D–A conjugation for optimized third-order NLO chromophores, an observation also made previously by others.¹⁴

H. Molecular Asymmetry. The significance of asymmetry in third-order NLO chromophores was initially postulated by Garito et al.,^{159,160} and this prediction has been confirmed experimentally for linearly conjugated molecules by us^{22,24} and others.^{62,83}

The four sets of chromophores **6–8**, **10–12**, **18–20**, and **29–31** clearly show increases in γ upon changing from centrosymmetric A–A or D–D substitution to acentric D–A substitution patterns. Considering the centrosymmetric molecules, the D–D substitution pattern seems favorable compared to A–A, leading to the heuristic rule for these one-dimensionally conjugated molecules:

$$\gamma(\text{A–A}) < \gamma(\text{D–D}) < \gamma(\text{A–D}) \quad (4)$$

This can be qualitatively shown by the symmetry of the electronic wave functions of the molecules. Assuming three electronic states contribute to the nonlinearity, the second hyperpolarizability γ can be approximated as^{22,159,160}

$$\gamma_{\text{cc}} = \underbrace{-\frac{(\mu_{01}^x)^4}{E_{01}^3}}_{=\text{N}} + \underbrace{\frac{(\mu_{01}^x)^2(\Delta\mu_1^x)^2}{E_{01}^3}}_{=\text{D}} + \underbrace{\frac{(\mu_{01}^x)^2(\mu_{12}^x)^2}{E_{02}E_{01}^2}}_{=\text{TP}} \quad (5)$$

where E_{0n} is the energy difference between the state n and the ground state ($n = 0$), μ_{nm} the transition dipole moment between the states n , m , and $\Delta\mu_n = \mu_{nn} - \mu_{00}$ the difference of the dipole moments in the state n and the ground state. Three different terms are contributing to the nonlinearity: the negative term N, the dipolar term D, and the two-photon term TP. Because nonvanishing dipole moments can only occur in asymmetric molecules, the dipolar term D likely explains the enhanced γ of the D–A substitution pattern.

Using the D–A-TEEs **24–26**, **36**, **37**, we could recently assess the importance of low molecular symmetry for two-dimensional conjugation, the first such correlation to the best of our knowledge.²² Considering symmetry in the conjugation plane (x , y) as defined in Figure 1, dipole moments in the y -direction are forbidden for **24**, in the x -direction for **26**, and in both directions for **25**. Consequently, **25** shows the lowest γ -value (890×10^{-36} esu). Owing to more efficient linear conjugation paths in x -direction relative to the y -direction (Figure 1), **24** exhibits a larger nonlinearity than **26** (2000 vs 1590×10^{-36} esu). This is even more significant, if one keeps in mind that the longest wavelength absorption maximum λ_{max} shifts from 486 nm for **24** to 520 nm for **26**. For this red-shift of

over 30 nm, one would expect a significant positive impact on γ from resonance enhancement, but this is obviously exceeded by symmetry relations.

In the case of **36**, the symmetry in the conjugation plane is completely broken and dipole moments in x - and y -direction can both contribute, leading to the largest nonlinearity observed for a tetrakis-substituted TEE (2550×10^{-36} esu). Adding a second thiophene ring, as in going from **36** to **37**, increases symmetry and decreases the γ -value (2200×10^{-36} esu), despite a concurrent red-shift in the absorption spectrum. Thus, as outlined herein for **24–26**, **36**, and **37**, low symmetry clearly supersedes resonance enhancement in increasing the nonlinearity γ in TEEs.

I. Oligomers. The THG measurements of unfunctionalized, linear TEE-derived oligomers **40a–c** have been investigated at 1.9 μm , as have those of structurally related DEE-derived molecules **3a–f**, **42**, and **43** (Table 3).^{19,25} The two series of compounds provide the first examples of oligomers and longer-chain polymers of the poly(triacetylene) (PTA) type, the third linearly conjugated polymers with a nonaromatic all-carbon backbone in the progression which starts with polyacetylene (PA) and poly(diacetylene) PDA (Figure 2) and ultimately leads to carbyne $[-(\text{C}\equiv\text{C})_n-]$. Although THG measurements for molecules **40a–c** were hampered owing to low solubility in chloroform, second hyperpolarizabilities of these molecules were found to be about an order of magnitude higher than those of the analogous oligomers **3a–c**. Clearly, the existence of the additional conjugation resulting from the pendant alkynes of **40a–c** contributes to enhanced γ -values, as was observed in the comparison of DEE and TEE chromophores (*vide supra*).

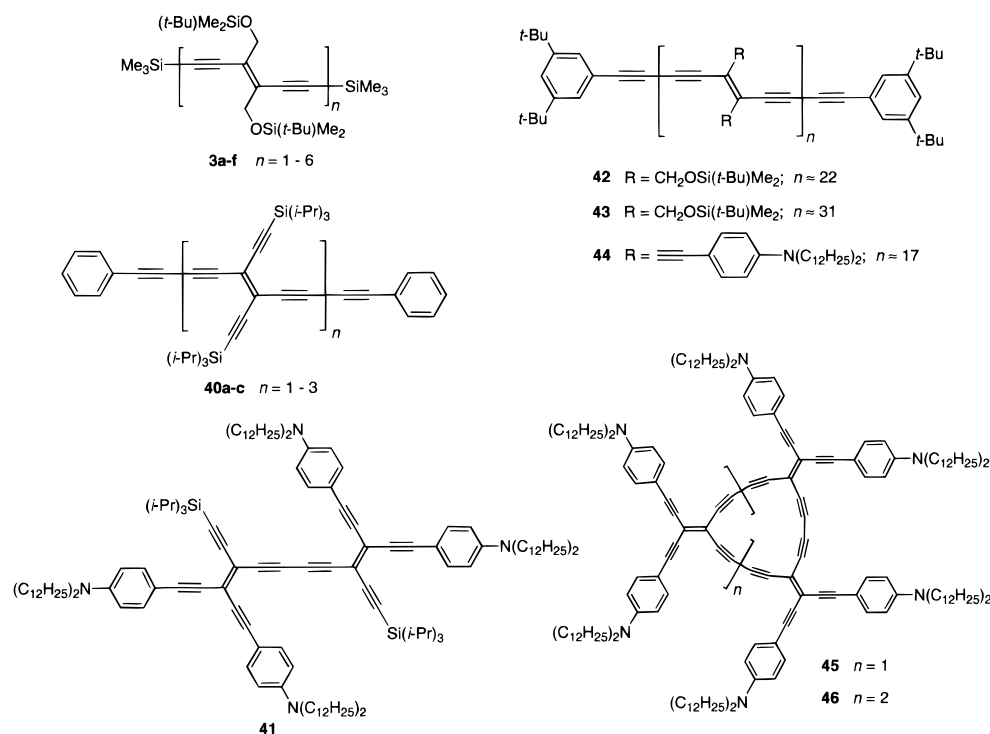
The increased solubility of the DEE oligomers **3a–f**, **42**, and **43**, resulting from pendent *tert*-butyldimethyl(silyloxy) groups, allowed a more comprehensive study of these molecules. For the rigid oligomers **3a–f**, γ -values steadily increased as a function of the length of the molecular rods, which extends between the terminal Si to Si atoms from 0.96 nm (**3a**) to 4.61 nm (**3f**). The exponential relationship for **3a–f** ($\gamma \propto N^n$) afforded $n = 2.5$, which is comparable to the exponent value for unsubstituted PA ($n = 2.5$).⁴⁷ THG measurements on a film sample of polydisperse PTA **43** consisting of an average of 31 monomeric subunits showed a macroscopic susceptibility $\chi^{(3)} = 6.0 \times 10^{-12}$ esu,²⁵ which was reproduced within 1% in solution for **42** with an average of 22 monomeric subunits, showing that saturation of γ had already been attained by this oligomer length. Using data from **3a–f**, **42**, and **43**, a critical conjugation length for γ of ca. 10 monomer units (30 double and triple bonds) was arrived at for these PTA oligomers, which is considerably shorter than that observed for γ in PAs which occurred only at about 120 double bonds.⁴⁷

The NLO properties of the electron-rich TEE dimer **41**, PTA polymer **44** with an average of 17 monomeric TEE subunits, and the cyclic oligomers **45–46**, which belong to the novel family of nonbenzenoid cyclic π -chromophores named as “expanded radialenes”, were investigated by THG at 2.1 μm .²³ It is interesting to note the evolution of second hyperpolarizabilities as a result of increased donor functionality in these oligomers. Assuming comparable contributions to γ from didodecyl- and dimethylamino groups as discussed for TEEs **27** and **28** (*vide supra*), then a comparison between dimers **30** and **41** (measured at 1.9 and 2.1 μm , respectively) plainly shows a significant increase in optical nonlinearity as a result of the two additional donor moieties in **41** (1900 vs 2900×10^{-36} esu). This is particularly interesting in view of the decreased wavelength of the lowest energy absorption maximum λ_{max} of **41** as compared

TABLE 3: Results of Third-Harmonic Generation Experiments for TEE and DEE Oligomers

	n	λ_{\max} [nm] ^a (ϵ) ^b	$\lambda(\omega)$ (μm)	ϵ at 3ω [mol/(cm dm ³)]	γ [10 ⁻³⁶ esu]	γ [10 ⁻⁴⁸ m ⁵ /V ²]	$(\chi^{(3)} 100\%)/\chi_{\text{fs}}^{(3)c}$
3a	1	296 ^d (19 700)	1.9	0	22	0.32	5
3b	2	378 ^d (24 200)	1.9	0	108	1.51	13
3c	3	420 ^d (28 600)	1.9	0	363	5.08	31
3d	4	439 ^d (35 200)	1.9	0	740	10.3	49
3e	5	459 ^d (29 700)	1.9	0	1320	18.5	72
3f	6	464 ^d (36 500)	1.9	0	1780	24.9	79
40a	1	422 (35 500)	1.9	0	240	3.41	41
40b	2	478 (31 000)	1.9	0	1030	14.5	105
40c	3	506 (51 500)	1.9	0	2570	35.9	183
41		479 (81 500)	2.1	0	2900	40	140
42	≈ 22	480 ^d	1.9	0	15 650	219	200
43	≈ 31	480 ^d	1.9	0	22 000	308	200
44	≈ 17	478 (55 200)	2.1	11 400	71 000	980	860
45	1	646 (171 000)	2.1	27 300	43 000	610	2700
46	2	574 (144 500)	2.1	12 400	17 000	240	800

^a λ_{\max} is the longest wavelength electronic absorption maximum as measured in CHCl₃. ^b Molar extinction coefficient. ^c $\chi^{(3)}$ of fused silica (fs), for which a value of $\chi^{(3)} = 3.9 \times 10^{-22} \text{ m}^2/\text{V}^2$ (2.8×10^{-14} esu) has been used; see ref 146. ^d Values obtained by deconvolution of the absorption spectra; see ref 19.



to **30** (479 and 486 nm, respectively) and an expected lowering of γ for **41** as a result of dispersion at the longer THG wavelength.

A comparison of the electronic absorption spectra of **41** and **45–46** shows the absorption onset for expanded radialenes **45** and **46** (ca. 730 nm) to be about 100 nm lower in energy than for dimer **41** (ca. 630 nm). It is probable that macrocyclic cross-conjugation contributes to the π -electron delocalization in the

expanded radialenes, a fact that is expected to significantly enhance γ for the cyclic structures. Indeed, the second hyperpolarizabilities γ of the electron-rich radialenes **45** and **46**, as well as that for PTA **44**, are huge compared to those measured for the corresponding donor functionalized monomeric TEEs (such as **14**, **16**, or **19**) or dimeric TEEs (such as **30** and **41**). Even the macroscopic $\chi^{(3)}$, which expresses the nonlinearity per unit volume, yields an increase of about 1 order of

magnitude. The γ - and $\chi^{(3)}$ -values obtained for radialenes **45**–**46** are comparable to or higher than the values measured for other conjugated, macrocyclic materials such as porphyrins^{161,162} and phthalocyanines.^{163–172} For example, phthalocyanines exhibit γ -values up to $45\,700 \times 10^{-36}$ esu (THG at $1.34\,\mu\text{m}$),¹⁷³ a silicon naphthalocyanine showed $\gamma = 3140 \times 10^{-36}$ esu (THG at $1.9\,\mu\text{m}$),¹⁷⁴ and metallotriazolohemiporphyrines have γ -values in a range of $(100\text{--}1000) \times 10^{-36}$ esu (THG at 1.3 or $1.9\,\mu\text{m}$).¹⁷⁵ For metallo(bis-phthalocyanines), second hyperpolarizabilities up to $480\,000 \times 10^{-36}$ esu were measured by DFWM, with individual values being strongly dependent upon the nature of the metal ion.¹⁷⁶ All three oligomeric compounds **44**–**46**, however, are strongly absorbing at the third harmonic frequency (700 nm), as are the other macrocyclic systems discussed here. This affords resonantly enhanced γ -values, and more meaningful comparisons between these materials are therefore difficult without an appropriate dispersion model.

The projected bulk third-order nonlinear optical susceptibilities for the expanded radialenes **45**–**46** (e.g., **45**: $\chi^{(3)} = 7.6 \times 10^{-11}$ esu) are comparable to those of several reported macrocycles measured by THG as thin films, including phthalocyanines with $\chi^{(3)}$ up to 5×10^{-11} esu¹⁷⁷ and oligomeric phthalocyanato(ruthenium(II)) complexes with $\chi^{(3)} = 0.37 \times 10^{-11}$ esu.¹⁷⁸ The values of $\chi^{(3)}$ for **45**–**46** are, however, considerably lower than those reported by Anderson et al. for linear conjugated rods consisting of porphyrins rigidly linked by buta-1,3-diynediynyl tethers.¹⁷⁹ It should be noted that use of widely differing experimental conditions and methods makes this comparison of $\chi^{(3)}$ results for macrocyclic systems qualitative, at best.¹²

These results provide encouragement that attributes found to be important in the optimization of the second hyperpolarizability γ in monomeric and dimeric TEEs can indeed be incorporated into potentially useful oligomeric and polymeric NLO materials. Routes toward improved oligomeric and polymeric NLO systems derived from TEEs and DEEs are currently being investigated.

5. Summary and Conclusions

The structure–function relationships for organic and organometallic third-order nonlinear optical materials as summarized herein highlight recent achievements in the development of new NLO-active chromophores, as well as the diverse range of chromophores that has been investigated. These studies have substantially broadened our understanding of the fundamental structural characteristics that are critical to increased NLO responses. Despite these efforts, however, organic compounds with nonlinear susceptibilities sufficient for practical applications remain elusive. It is becoming clear that simply manipulating and improving traditional one-dimensional chromophoric systems will not likely afford materials with optical nonlinearities and stabilities adequate for devices. For linearly conjugated oligomers and polymers such as polythiophene, polyenes, or polyyenes, a number of studies outlined herein suggest or have shown that γ and $\chi^{(3)}$ will reach saturation as a function of conjugation length before acceptable values are achieved. Thus, additional design elements and improvements must be developed and realized.

We have utilized the sterically unencumbered frameworks of diethynylethenes (DEEs) and tetraethynylethenes (TEEs) to probe changes in the second hyperpolarizability γ as a result of both subtle and major structural modifications. Our THG studies of functionalized DEEs and TEEs have furnished a number of new and important criteria for the optimization of

molecular third-order nonlinearities. First and foremost, the fully two-dimensionally conjugated TEE framework is critical to providing significant γ -values. By synthetically manipulating substituents about the TEE skeleton, it could be shown that extended conjugation length and donor strength can also be exploited to further enhance the second hyperpolarizability in these molecules. These structural modifications include the incorporation of strong *N,N*-dialkylaminophenyl donors, heteroaromatic rather than phenyl subchromophores, and extension of molecular structure to dimeric TEE derivatives. The subtle effects of donor–acceptor stereochemistry on γ -values have also been elucidated, and, for TEEs and DEEs, the D–A charge-transfer efficiency and γ decrease in the series as *trans* > *cis* >> *geminal*.

Molecular acentricity has been determined as essential for achieving significantly increased γ -values. Our results with linearly conjugated, one-dimensional TEEs and DEEs concur with predictions of Garito et al. that D–A acentricity across a conjugated framework affords marked gains in third-order optical nonlinearities. The effects of low symmetry with regard to conjugation path are even more dramatic in fully two-dimensionally conjugated tetrakis-arylated TEEs. In this case, the observed gains in nonlinearities could be explained by considering symmetry rules, which ultimately determine the dipolar contributions to the second hyperpolarizabilities.

We conclude that two-dimensional conjugation and low symmetry are likely the two most powerful tools for optimizing the second hyperpolarizability γ in small molecules. By using symmetry effects to increase dipolar contributions, in combination with tuning of the NLO properties through variation of donor/acceptor strength, bond length alternation, or conjugation paths, the prospects for optimized, useful third-order NLO chromophores are promising. Current efforts strive to control and refine the assembly of individual TEE “building blocks” into environmentally stable, processable structured oligomers and polymers such as poly(triacetylene)s and expanded radialenes, which appear to be viable materials for NLO applications.

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References and Notes

- (1) *Nonlinear Optics of Organic Molecules and Polymers*; Nalwa, H. S., Miyata, S., Eds.; CRC Press: Boca Raton, FL, 1997.
- (2) *Nonlinear Optical Materials: Theory and Modeling*; Karna, S. P.; Yeates, A. Y., Eds.; American Chemical Society: Washington, DC, 1996.
- (3) Zyss, J.; Nicoud, J.-F. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 533–546.
- (4) Bosshard, C.; Sutter, K.; Prêtre, P.; Hulliger, J.; Flörsheimer, M.; Kaatz, P.; Günter, P. *Organic Nonlinear Optical Materials*; Gordon and Breach: Basel, 1995.
- (5) Special issues: *Chem. Rev.* **1994**, *94*, 1–278; *J. Opt. Soc. Am. B* **1998**, *15*, 723–932.
- (6) Zyss, J. *Molecular Nonlinear Optics: Materials, Physics and Devices*; Academic Press: Boston, 1993.
- (7) *Organic Materials for Nonlinear Optics II*; Hann, R. A., Bloor, D., Eds.; The Royal Society of Chemistry: Cambridge, 1991.
- (8) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991.
- (9) *Nonlinear Optical Properties of Polymers: Materials Research Society Symposium Proceedings*; Heeger, A. J., Orenstein, J., Ulrich, D. R., Eds.; Materials Research Society: Pittsburgh, PA, 1988; Vol. 109.
- (10) *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: Orlando, FL, 1987.
- (11) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690–703.
- (12) Willetts, A.; Rice, J. E.; Burland, D. M.; Shelton, D. P. *J. Chem. Phys.* **1992**, *97*, 7590–7599.

- (13) Boyd, G. T. *J. Opt. Soc. Am. B* **1989**, 6, 685–692.
- (14) Nalwa, H. S. *Adv. Mater.* **1993**, 5, 341–358.
- (15) Wytko, J.; Martin, R. E.; Tykwinski, R. R.; Diederich, F.; Seiler, P.; Gramlich, V.; Gisselbrecht, J.-P.; Boudon, C.; Gross, M. In preparation.
- (16) For photochemical *trans-cis* isomerizations in D/A-substituted DEEs and TEEs, see: Martin, R. E.; Bartek, J.; Diederich, F.; Tykwinski, R. R.; Meister, E.; Hilger, A.; Lüthi, H. P. *J. Chem. Soc., Perkin Trans. 2* **1998**, 233–241.
- (17) For a survey of the synthesis of DEEs and TEEs, see: Tykwinski, R. R.; Diederich, F. *Liebigs Ann./Recueil* **1997**, 649–661.
- (18) For the electronic and electrochemical properties of D/A-substituted DEEs and TEEs, see: Hilger, A.; Gisselbrecht, J.-P.; Tykwinski, R. R.; Boudon, C.; Schreiber, M.; Martin, R. E.; Lüthi, H. P.; Gross, M.; Diederich, F. *J. Am. Chem. Soc.* **1997**, 119, 2069–2078.
- (19) Martin, R. E.; Gubler, U.; Boudon, C.; Gramlich, V.; Bosshard, C.; Gisselbrecht, J.-P.; Günter, P.; Gross, M.; Diederich, F. *Chem. Eur. J.* **1997**, 3, 1505–1512.
- (20) Tykwinski, R. R.; Schreiber, M.; Pérez Carlón, R.; Diederich, F.; Gramlich, V. *Helv. Chim. Acta* **1996**, 79, 2249–2281.
- (21) Tykwinski, R. R.; Schreiber, M.; Gramlich, V.; Seiler, P.; Diederich, F. *Adv. Mater.* **1996**, 8, 226–231.
- (22) Gubler, U.; Spreiter, R.; Bosshard, C.; Günter, P.; Tykwinski, R. R.; Diederich, F. *Phys. Rev. Lett.*, submitted.
- (23) Schreiber, M.; Tykwinski, R. R.; Diederich, F.; Spreiter, R.; Gubler, U.; Bosshard, C.; Poberaj, I.; Günter, P.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M.; Jonas, U.; Ringsdorf, H. *Adv. Mater.* **1997**, 9, 339–343.
- (24) Bosshard, C.; Spreiter, R.; Günter, P.; Tykwinski, R. R.; Schreiber, M.; Diederich, F. *Adv. Mater.* **1996**, 8, 231–234.
- (25) Schreiber, M.; Anthony, J.; Diederich, F.; Spahr, M. E.; Nesper, R.; Hubrich, M.; Bommeli, F.; Degiorgi, L.; Wachter, P.; Kaatz, P.; Bosshard, C.; Günter, P.; Colussi, M.; Suter, U. W.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M. *Adv. Mater.* **1994**, 6, 786–790.
- (26) Nalwa, H. S. In *Nonlinear Optics of Organic Molecules and Polymers*; Nalwa, H. S., Miyata, S., Eds.; CRC Press: Boca Raton, FL, 1997; pp 611–797.
- (27) Hermann, J.-P.; Ducuing, J. *J. Appl. Phys.* **1974**, 45, 5100–5102.
- (28) Levine, B. F.; Betha, C. G. *J. Chem. Phys.* **1975**, 63, 2666–2682.
- (29) Kost, D.; Yeates, A. T.; Dudis, D. S. *J. Chem. Soc., Chem. Commun.* **1993**, 83–84.
- (30) Kajzar, F.; Messier, J. *J. Opt. Soc. Am. B* **1987**, 4, 1040–1046.
- (31) Kajzar, F.; Messier, J. *Phys. Rev. A* **1985**, 32, 2352–2363.
- (32) Meredith, G. R.; Buchalter, B.; Hanzlik, C. *J. Chem. Phys.* **1983**, 78, 1533–1542.
- (33) Hermann, J.-P.; Ricard, D.; Ducuing, J. *Appl. Phys. Lett.* **1973**, 23, 178–180.
- (34) Agrawal, G. P.; Cojan, C.; Flytzanis, C. *Phys. Rev. B* **1978**, 17, 776–789.
- (35) Sauteret, C.; Hermann, J.-P.; Frey, R.; Pradère, F.; Ducuing, J.; Baughman, R. H.; Chance, R. R. *Phys. Rev. Lett.* **1976**, 36, 956–959.
- (36) Cha, M.; Torruellas, W. E.; Yuan, S. H.; Stegeman, G. I.; Leclerc, M. *J. Opt. Soc. Am. B* **1995**, 12, 882–888.
- (37) Torruellas, W. E.; Neher, D.; Zanon, R.; Stegeman, G. I.; Kajzar, F.; Leclerc, M. *Chem. Phys. Lett.* **1990**, 175, 11–16.
- (38) Soos, Z. G.; Ramasesha, S. *J. Chem. Phys.* **1989**, 90, 1067–1076.
- (39) Chopra, P.; Caracci, L.; King, H. F.; Prasad, P. N. *J. Phys. Chem.* **1989**, 93, 3, 7120–7130.
- (40) Pierce, B. M. *J. Chem. Phys.* **1989**, 91, 791–811.
- (41) Prasad, P. N.; Perrin, E.; Samoc, M. *J. Chem. Phys.* **1989**, 91, 2360–2365.
- (42) de Melo, C. P.; Silbey, R. *J. Chem. Phys.* **1988**, 88, 2567–2571.
- (43) Zhao, M.-T.; Singh, B. P.; Prasad, P. N. *J. Chem. Phys.* **1988**, 89, 5535–5541.
- (44) Beratan, D. N.; Onuchic, J. N.; Perry, J. W. *J. Phys. Chem.* **1987**, 91, 2696–2698.
- (45) Zamani-Khamiri, O.; Hameka, H. F. *J. Chem. Phys.* **1980**, 73, 5693–5697.
- (46) Craig, G. S. W.; Cohen, R. E.; Schrock, R. R.; Silbey, R. J.; Puccetti, G.; Ledoux, I.; Zyss, J. *J. Am. Chem. Soc.* **1993**, 115, 860–867.
- (47) Samuel, I. D. W.; Ledoux, I.; Dhenaut, C.; Zyss, J.; Fox, H. H.; Schrock, R. R.; Silbey, R. J. *Science (Washington, D.C.)* **1994**, 265, 1070–1072.
- (48) Neher, D.; Kaltbeitzel, A.; Wolf, A.; Bubeck, C.; Wegner, G. *J. Phys. D: Appl. Phys.* **1991**, 24, 1193–1202.
- (49) Rumi, M.; Zerbi, G.; Müllen, K.; Müller, G.; Rehahn, M. *J. Chem. Phys.* **1997**, 106, 24–34.
- (50) Mathy, A.; Ueberhofen, K.; Schenk, R.; Gregorius, H.; Garay, R.; Müllen, K.; Bubeck, C. *Phys. Rev. B* **1996**, 53, 4367–4376.
- (51) Fichou, D.; Garnier, F.; Charra, F.; Kajzar, F.; Messier, J. In *Organic Materials for Nonlinear Optics*; Hann, R. A., Bloor, D., Eds.; The Royal Society of Chemistry: London, 1989; pp 176–182.
- (52) Cheng, L.-T.; Tour, J. M.; Wu, R.; Bedworth, P. V. *Nonlinear Opt.* **1993**, 6, 87–92.
- (53) Thienpont, H.; Rikken, G. L. J. A.; Meijer, E. W.; ten Hoeve, W.; Wynberg, H. *Phys. Rev. Lett.* **1990**, 65, 2141–2144.
- (54) Björnholm, T.; Greve, D. R.; Geisler, T.; Petersen, J. C.; Jayaraman, M.; McCullough, R. D. *Synth. Met.* **1997**, 84, 531–532.
- (55) Björnholm, T.; Greve, D. R.; Geisler, T.; Petersen, J. C.; Jayaraman, M.; McCullough, R. D. *Adv. Mater.* **1996**, 8, 920–923.
- (56) Schrof, W.; Rozouvan, S.; Hartmann, T.; Möhwald, H.; Belov, V.; Van Keuren, E. *J. Opt. Soc. Am. B* **1998**, 15, 889–894.
- (57) Samuel, I. D. W.; Ledoux, I.; Delporte, C.; Pearson, D. L.; Tour, J. M. *Chem. Mater.* **1996**, 8, 819–821.
- (58) Geisler, T.; Petersen, J. C.; Björnholm, T.; Fischer, E.; Larsen, J.; Dehu, C.; Brédas, J.-L.; Tormos, G. V.; Nugara, P. N.; Cava, M. P.; Metzger, R. M. *J. Phys. Chem.* **1994**, 98, 10102–10111.
- (59) Ooba, N.; Tomaru, S.; Kurihara, T.; Kaino, T.; Yamada, W.; Takagi, M.; Yamamoto, T. *Jpn. J. Appl. Phys. 1* **1995**, 34, 3139–3141.
- (60) Kaino, T.; Ooba, N.; Tomaru, S.; Kurihara, T.; Yamamoto, T. *Mater. Res. Soc. Symp. Proc.* **1994**, 328, 449–460.
- (61) Zhao, M.-T.; Samoc, M.; Singh, B. P.; Prasad, P. N. *J. Phys. Chem.* **1989**, 93, 3, 7916–7920.
- (62) Spangler, C. W.; Havelka, K. O.; Becker, M. W.; Kelleher, T. A.; Cheng, L.-T. *Proc. SPIE-Int. Soc. Opt. Eng.* **1991**, 1560, 139–147.
- (63) Cheng, L.-T.; Tam, W.; Stevenson, S. H.; Meredith, G. R.; Rikken, G.; Marder, S. R. *J. Phys. Chem.* **1991**, 95, 10631–10643.
- (64) Wautelet, P.; Moroni, M.; Oswald, L.; Le Moigne, J.; Pham, A.; Bigot, J.-Y.; Luzzati, S. *Macromolecules* **1996**, 29, 446–455.
- (65) Reinhardt, B. A. *Trends Polym. Sci.* **1993**, 1, 4–9.
- (66) Nalwa, H. S.; Hamada, T.; Kakuta, A.; Mukoh, A. *Jpn. J. Appl. Phys. 2* **1993**, 32, L193–L196.
- (67) Werncke, W.; Pfeiffer, M.; Lau, A.; Grahn, W.; Johannes, H.-H.; Dähne, L. *J. Opt. Soc. Am. B* **1998**, 15, 863–870.
- (68) Johr, T.; Werncke, W.; Pfeiffer, M.; Lau, A.; Dähne, L. *Chem. Phys. Lett.* **1995**, 246, 521–526.
- (69) Matsumoto, S.; Kubodera, K.; Kurihara, T.; Kaino, T. *Opt. Commun.* **1990**, 76, 147–150.
- (70) Stevenson, S. H.; Donald, D. S.; Meredith, G. R. *Mater. Res. Soc. Proc. Symp.* **1988**, 109, 103–108.
- (71) Perry, J. W.; Stiegman, A. E.; Marder, S. R.; Coulter, D. R. In *Organic Materials for Nonlinear Optics*; Hann, R. A., Bloor, D., Eds.; The Royal Society of Chemistry: London, 1989; pp 189–195.
- (72) Gorman, C. B.; Marder, S. R. *Chem. Mater.* **1995**, 7, 215–220.
- (73) Marder, S. R.; Gorman, C. B.; Meyers, F.; Perry, J. W.; Bourhill, G.; Brédas, J.-L.; Pierce, B. M. *Science (Washington, D.C.)* **1994**, 265, 632–635.
- (74) Meyers, F.; Marder, S. R.; Pierce, B. M.; Brédas, J.-L. *J. Am. Chem. Soc.* **1994**, 116, 10703–10714.
- (75) Marder, S. R.; Perry, J. W.; Bourhill, G.; Gorman, C. B.; Tiemann, B. G.; Mansour, K. *Science (Washington, D.C.)* **1993**, 261, 186–189.
- (76) Gorman, C. B.; Marder, S. R. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, 90, 11297–11301.
- (77) Lu, D.; Chen, G.; Perry, J. W.; Goddard III, W. A. *J. Am. Chem. Soc.* **1994**, 116, 10679–10685.
- (78) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, 66, 2664–2668.
- (79) Oudar, J. L.; Chemla, D. S.; Batifol, E. *J. Chem. Phys.* **1977**, 67, 1626–1635.
- (80) Oudar, J. L. *J. Chem. Phys.* **1977**, 67, 446–457.
- (81) Cheng, L.-T.; Tam, W.; Marder, S. R.; Stiegman, A. E.; Rikken, G.; Spangler, C. W. *J. Phys. Chem.* **1991**, 95, 10643–10652.
- (82) Beljonne, D.; Cornil, J.; Shuai, Z.; Brédas, J.-L.; Rohlfling, F.; Bradley, D. D. C.; Torruellas, W. E.; Ricci, V.; Stegeman, G. I. *Phys. Rev. B* **1997**, 55, 1505–1516.
- (83) Marder, S. R.; Torruellas, W. E.; Blanchard-Desce, M.; Ricci, V.; Stegeman, G. I.; Gilmour, S.; Brédas, J.-L.; Li, J.; Bubltz, G. U.; Boxer, S. G. *Science (Washington, D.C.)* **1997**, 276, 1233–1236.
- (84) Blanchard-Desce, M.; Lehn, J.-M.; Barzoukas, M.; Runser, C.; Fort, A.; Puccetti, G.; Ledoux, I.; Zyss, J. *Nonlinear Opt.* **1995**, 10, 23–36.
- (85) Esser, A.; Fisch, H.; Haas, K. H.; Hädicke, E.; Paust, J.; Schrof, W.; Tickin, A. In *Organic Materials for Nonlinear Optics III*; Ashwell, G. J., Bloor, D., Eds.; The Royal Society of Chemistry: Cambridge, 1993; pp 213–218.
- (86) Puccetti, G.; Blanchard-Desce, M.; Ledoux, I.; Lehn, J.-M.; Zyss, J. *J. Phys. Chem.* **1993**, 97, 9385–9391.
- (87) Messier, J.; Kajzar, F.; Sentein, C.; Barzoukas, M.; Zyss, J.; Blanchard-Desce, M.; Lehn, J.-M. *Nonlinear Opt.* **1992**, 2, 53–70.
- (88) Aramaki, S.; Torruellas, W.; Zanon, R.; Stegeman, G. I. *Opt. Commun.* **1991**, 85, 527–535.
- (89) van Beek, J. B.; Kajzar, F.; Albrecht, A. C. *J. Chem. Phys.* **1991**, 95, 6400–6412.
- (90) Heflin, J. R.; Cai, Y. M.; Garito, A. F. *J. Opt. Soc. Am. B* **1991**, 8, 2132–2147.
- (91) Zhao, M.; Samoc, M.; Prasad, P. N.; Reinhardt, B. A.; Unroe, M. R.; Prazak, M.; Evers, R. C.; Kane, J. J.; Jariwala, C.; Sinsky, M. *Chem. Mater.* **1990**, 2, 670–678.
- (92) Prasad, P. N.; Reinhardt, B. A. *Chem. Mater.* **1990**, 2, 660–669.

- (93) Kminek, I.; Klimovic, J.; Prasad, P. N. *Chem. Mater.* **1993**, 5, 357–360.
- (94) Ermer, S.; Lovejoy, S.; Leung, D.; Altman, J.; Aron, K.; Spitzer, R.; Hansen, G. *Proc. SPIE-Int. Soc. Opt. Eng.* **1990**, 1337, 89–98.
- (95) Dirk, C. W.; Cheng, L.-T.; Kuzyk, M. G. *Int. J. Quantum Chem.* **1992**, 43, 27–36.
- (96) Dirk, C. W.; Herndon, W. C.; Cervantes-Lee, F.; Selna, H.; Martinez, S.; Kalamegham, P.; Tan, A.; Campos, G.; Velez, M.; Zyss, J.; Ledoux, I.; Cheng, L.-T. *J. Am. Chem. Soc.* **1995**, 117, 2214–2225.
- (97) Tran, K.; Scott, G. W.; Funk, D. J.; Moore, D. S. *J. Phys. Chem.* **1996**, 100, 0, 11863–11869.
- (98) Gabriel, M. C.; Whitaker Jr., N. A.; Dirk, C. W.; Kuzyk, M. G.; Thakur, M. *Opt. Lett.* **1991**, 16, 1334–1336.
- (99) Kuzyk, M. G.; Sohn, J. E.; Dirk, C. W. *J. Opt. Soc. Am. B* **1990**, 7, 842–858.
- (100) Poga, C.; Brown, T. M.; Kuzyk, M. G.; Dirk, C. W. *J. Opt. Soc. Am. B* **1995**, 12, 531–543.
- (101) Andrews, J. H.; Khaydarov, J. D. V.; Singer, K. D. *J. Opt. Soc. Am. B* **1995**, 12, 2360–2371.
- (102) Andrews, J. H.; Khaydarov, J. D. V.; Singer, K. D.; Hull, D. L.; Chuang, K. C. *Nonlinear Opt.* **1995**, 10, 227–238.
- (103) Yu, Y. Z.; Shi, R. F.; Garito, A. F.; Grossman, C. H. *Opt. Lett.* **1994**, 19, 786–788.
- (104) Mathis, K. S.; Kuzyk, M. G.; Dirk, C. W.; Tan, A.; Martinez, S.; Gampos, G. *J. Opt. Soc. Am. B* **1998**, 15, 871–883.
- (105) Gotoh, T.; Kondoh, T.; Egawa, K.; Kubodera, K. *J. Opt. Soc. Am. B* **1989**, 6, 703–706.
- (106) Huggard, P. G.; Blau, W.; Schweitzer, D. *Appl. Phys. Lett.* **1987**, 51, 2183–2185.
- (107) Gong, Q.; Xia, Z.; Zou, Y. H.; Meng, X.; Wei, M.; Li, F. *Appl. Phys. Lett.* **1991**, 59, 381–383.
- (108) Kondo, K.; Yasuda, S.; Sakaguchi, T.; Miya, M. *J. Chem. Soc., Chem. Commun.* **1995**, 55–56.
- (109) Sahraoui, B.; Sylla, M.; Bourdin, J. P.; Rivoire, G.; Zaremba, J.; Nguyen, T. T.; Sallé, M. *J. Mod. Opt.* **1995**, 42, 2095–2107. Sahraoui, B.; Rivoire, G.; Terkia-Derdra, N.; Sallé, M.; Zaremba, J. *J. Opt. Soc. Am. B* **1998**, 15, 923–928.
- (110) Takahashi, M.; Yamada, S.; Matsuda, H.; Nakanishi, H.; Tsuchida, E.; Nishide, H. *J. Chem. Soc., Chem. Commun.* **1997**, 1853–1854.
- (111) Rustagi, K. C.; Nair, S. V.; Ramaniah, L. M. *Prog. Cryst. Growth and Charact.* **1997**, 34, 81–93. See also: Huang, H.; Gu, G.; Yang, S.; Fu, J.; Yu, P.; Wong, G. K. L.; Du, Y. *J. Phys. Chem. B* **1998**, 102, 61–66. Kanbara, H.; Maruno, T.; Yamashita, A.; Matsumoto, S.; Hayashi, T. *J. Appl. Phys.* **1996**, 80, 3674–3682.
- (112) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 21–38.
- (113) Nalwa, H. S. *Appl. Organomet. Chem.* **1991**, 5, 349–377.
- (114) Winter, C. S.; Oliver, S. N.; Rush, J. D. In *Organic Materials for Nonlinear Optics*; Hann, R. A., Bloor, D., Eds.; The Royal Society of Chemistry: London, 1989; pp 232–237.
- (115) Winter, C. S.; Oliver, S. N.; Rush, J. D.; Manning, R. J.; Hill, C.; Underhill, A. In *Materials for Nonlinear Optics: Chemical Perspectives*; Marder, S. R., Sohn, J. E., Stucky, G. D., Eds.; American Chemical Society: Washington, DC, 1991; Vol. 455, pp 616–625.
- (116) Myers, L. K.; Ho, D. M.; Thompson, M. E.; Langhoff, C. *Polyhedron* **1995**, 14, 57–67.
- (117) Schougaard, S. B.; Greve, D. R.; Geisler, T.; Petersen, J. C.; Bjørnholm, T. *Synth. Met.* **1997**, 86, 2179–2180.
- (118) Sachtleben, M. L.; Spangler, C. W.; Tang, N.; Hellwarth, R.; Dalton, L. In *Organic Materials for Nonlinear Optics III*; Aswell, G. J., Bloor, D., Eds.; The Royal Society of Chemistry: Cambridge, 1993; pp 231–236.
- (119) Yuan, Z.; Stringer, G.; Jobe, I. R.; Kreller, D.; Scott, K.; Koch, L.; Taylor, N. J.; Marder, T. B. *J. Organomet. Chem.* **1993**, 452, 115–120.
- (120) Ghosal, S.; Samoc, M.; Prasad, P. N.; Tufariello, J. J. *J. Phys. Chem.* **1990**, 94, 2847–2851.
- (121) Winter, C. S.; Oliver, S. N.; Rush, J. D. *Opt. Commun.* **1988**, 69, 45–48.
- (122) Whittall, I. R.; Humphrey, M. G.; Samoc, M.; Swiatkiewicz, J.; Luther-Davies, B. *Organometallics* **1995**, 14, 5493–5495.
- (123) McDonagh, A. M.; Cifuentes, M. P.; Whittall, I. R.; Humphrey, M. G.; Samoc, M.; Luther-Davies, B.; Hockless, D. C. R. *J. Organomet. Chem.* **1996**, 526, 99–103.
- (124) Whittall, I. R.; Humphrey, M. G.; Samoc, M.; Luther-Davies, B. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 370–371.
- (125) Dias, A. R.; Garcia, M.-H.; Rodrigues, J. C.; Petersen, J. C.; Bjørnholm, T.; Geisler, T. *J. Mater. Chem.* **1995**, 5, 1861–1865.
- (126) Kamata, T.; Fukaya, T.; Matsuda, H.; Mizukami, F.; Tachiya, M.; Ishikawa, R.; Uchida, T. *J. Phys. Chem.* **1995**, 99, 13239–13246.
- (127) Blau, W. J.; Byrne, H. J.; Cardin, D. J.; Davey, A. P. *J. Mater. Chem.* **1991**, 1, 245–249.
- (128) Guha, S.; Frazier, C. C.; Porter, P. L.; Kang, K.; Finberg, S. E. *Opt. Lett.* **1989**, 14, 952–954.
- (129) Frazier, C. C.; Chauchard, E. A.; Cockerham, M. P.; Porter, P. L. *Mater. Soc. Res. Symp. Proc.* **1988**, 109, 323–328.
- (130) Frazier, C. C.; Guha, S.; Chen, W. P.; Cockerham, M. P.; Porter, P. L.; Chauchard, E. A.; Lee, C. H. *Polymer* **1987**, 28, 553–555.
- (131) Porter, P. L.; Guha, S.; Kang, K.; Frazier, C. C. *Polymer* **1991**, 32, 1756–1760.
- (132) Greve, D. R.; Schougaard, S. B.; Geisler, T.; Peterson, J. C.; Bjørnholm, T. *Adv. Mater.* **1997**, 9, 1113–1116.
- (133) Bjørnholm, T. *Isr. J. Chem.* **1996**, 36, 349–356.
- (134) Brédas, J.-L.; Adant, C.; Tackx, P.; Persoons, A. *Chem. Rev.* **1994**, 94, 243–278.
- (135) Abe, J.; Shirai, Y.; Nemoto, N.; Nagase, Y.; Iyoda, T. *J. Phys. Chem. B* **1997**, 101, 145–149.
- (136) Thomas, R. J. *Chem. Soc., Perkin Trans 2* **1994**, 2137–2140.
- (137) Lee, S.-L.; Yang, K.-C.; Sheu, J.-H.; Lu, Y.-J. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1995**, 29, 509–522.
- (138) Adant, C.; Brédas, J.-L.; Dupuis, M. *J. Phys. Chem. A* **1997**, 101, 3025–3031.
- (139) Nalwa, H. S.; Mukai, J.; Kakuta, A. *J. Phys. Chem.* **1995**, 99, 10766–10774.
- (140) Matsuzaki, Y.; Nakano, M.; Yamaguchi, K.; Tanaka, K.; Yamabe, T. *Chem. Phys. Lett.* **1996**, 263, 119–125.
- (141) Wong, K. S.; Han, S. G.; Vardeny, Z. V.; Shinar, J.; Pang, Y.; Ijadi-Maghsoodi, S.; Barton, T. J.; Grigoros, S.; Parbhoo, B. *Appl. Phys. Lett.* **1991**, 58, 1695–1697.
- (142) Anthony, J.; Boldi, A. M.; Rubin, Y.; Hobi, M.; Gramlich, V.; Knobler, C. B.; Seiler, P.; Diederich, F. *Helv. Chim. Acta* **1995**, 78, 13–45.
- (143) Boldi, A. M.; Anthony, J.; Gramlich, V.; Knobler, C. B.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M.; Diederich, F. *Helv. Chim. Acta* **1995**, 78, 779–796.
- (144) Kajzar, F.; Ledoux, I.; Zyss, J. *Phys. Rev. A* **1987**, 36, 2210–2219.
- (145) Boettcher, C. J. *Theory of Electric Polarization*; Elsevier: Amsterdam, 1952.
- (146) Buchalter, B.; Meredith, G. R. *Appl. Opt.* **1982**, 21, 3221–3224.
- (147) Albert, I. D. L.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **1997**, 119, 9, 6575–6582.
- (148) Varanasi, P. R.; Jen, A. K.-Y.; Chandrasekhar, J.; Namboothiri, I. N. N.; Rathna, A. *J. Am. Chem. Soc.* **1996**, 118, 12443–12448.
- (149) Morley, J. O. *J. Chem. Soc., Faraday Trans.* **1991**, 87, 3009–3013.
- (150) de Lucas, A. I.; Martín, N.; Sánchez, L.; Seoane, C.; Garín, J.; Orduna, J.; Alcalá, R.; Villacampa, B. *Tetrahedron Lett.* **1997**, 38, 6107–6110.
- (151) Boldt, P.; Bourhill, G.; Bräuchle, C.; Jim, Y.; Kammler, R.; Müller, C.; Rase, J.; Wichern, J. *J. Chem. Soc., Chem. Commun.* **1996**, 793–795.
- (152) Rao, V. P.; Jen, A. K.-Y.; Cai, Y. *J. Chem. Soc., Chem. Commun.* **1996**, 1237–1238.
- (153) Wong, K. Y.; Jen, A. K.-Y.; Rao, V. P.; Drost, K. J. *Appl. Phys. B* **1995**, 61, 191–194.
- (154) Wong, M. S.; Meier, U.; Pan, F.; Gramlich, V.; Bosshard, C.; Günter, P. *Adv. Mater.* **1996**, 8, 416–420.
- (155) Spangler, C. S.; Kelleher, T. A.; Liu, P.-K.; Cheng, L.-T.; Tang, N.; Hellwarth, R. In *Organic Materials for Nonlinear Optics III*; Ashwell, G. J., Bloor, D., Eds.; The Royal Society of Chemistry: Cambridge, 1993; pp 19–24.
- (156) Kuzyk, M. G.; Dirk, C. W. *Appl. Phys. Lett.* **1989**, 54, 1628–1630.
- (157) Kamada, K.; Ueda, M.; Sakaguchi, T.; Ohta, K.; Fukumi, T. *J. Opt. Soc. Am. B* **1998**, 15, 838–845.
- (158) Bezerra, A. G., Jr.; Gomes, A. S. L.; de Melo, C. P.; de Araújo, C. B. *Chem. Phys. Lett.* **1997**, 276, 445–449.
- (159) Garito, A. F.; Heflin, J. R.; Wong, K. Y.; Zamani-Khamiri, O. In *Organic Materials for Nonlinear Optics*; Hann, R. A., Bloor, D., Eds.; The Royal Society of Chemistry: London, 1989; pp 16–27.
- (160) Wu, J. W.; Heflin, J. R.; Norwood, R. A.; Wong, K. Y.; Zamani-Khamiri, O.; Garito, A. F.; Kalyanaraman, P.; Sounik, J. *J. Opt. Soc. Am. B* **1989**, 6, 707–720.
- (161) Norwood, R. A.; Sounik, J. R. *Appl. Phys. Lett.* **1992**, 60, 295–297.
- (162) Rao, D. V. G. L. N.; Aranda, F. J.; Roach, J. F.; Remy, D. E. *Appl. Phys. Lett.* **1991**, 58, 1241–1243.
- (163) Tian, M.; Yanagi, S.; Sasaki, K.; Wada, T.; Sasabe, H. *J. Opt. Soc. Am. B* **1998**, 15, 846–853.
- (164) Yamashita, A.; Matsumoto, S.; Sakata, S.; Hayashi, T.; Kanbara, H. *Opt. Commun.* **1998**, 145, 141–144.
- (165) Nalwa, H. S.; Shirik, J. S. In *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH Publishers: New York, 1996; Vol. 4, pp 79–181.
- (166) Nalwa, H. S.; Kakuta, A. *Thin Solid Films* **1995**, 254, 218–223.
- (167) Nalwa, H. S.; Kakuta, A.; Mukoh, A. *J. Phys. Chem.* **1993**, 97, 7, 1097–1100.

- (168) Nalwa, H. S.; Saito, T.; Kakuta, A.; Iwayanagi, T. *J. Phys. Chem.* **1993**, 97, 10515–10517.
- (169) Nalwa, H. S.; Kobayashi, S.; Kakuta, A. *Nonlinear Opt.* **1993**, 6, 169–179.
- (170) Shirk, J. S.; Lindle, J. R.; Bartoli, F. J.; Boyle, M. E. *J. Phys. Chem.* **1992**, 96, 5847–5852.
- (171) Matsuda, H.; Okada, S.; Masaki, A.; Nakanishi, H.; Suda, Y.; Shigehara, K.; Yamada, A. *SPIE-Int. Soc. Opt. Eng.* **1990**, 1337, 105–113.
- (172) Shirk, J. S.; Lindle, J. R.; Bartoli, F. J.; Hoffman, C. A.; Kafafi, Z. H.; Snow, A. W. *Appl. Phys. Lett.* **1989**, 55, 1287–1288.
- (173) Días-García, M. A.; Ledoux, I.; Duro, J. A.; Torres, T.; Agulló-López, F.; Zyss, J. *J. Phys. Chem.* **1994**, 98, 8761–8764.
- (174) Wang, N. Q.; Cai, Y. M.; Heflin, J. R.; Garito, A. F. *Mol. Cryst. Liq. Cryst.* **1990**, 189, 39–48.
- (175) Días-García, M. A.; Ledoux, I.; Fernández-Lázaro, F.; Sastre, A.; Torres, T.; Agulló-López, F.; Zyss, J. *J. Phys. Chem.* **1994**, 98, 4495–4497.
- (176) Shirk, J. S.; Lindle, J. R.; Bartoli, F. J.; Kafafi, Z. H.; Snow, A. W.; Boyle, M. E. *Int. J. Nonlinear Opt. Phys.* **1992**, 1, 699–726.
- (177) Ho, Z. Z.; Ju, C. Y.; Hetherington III, W. M. *J. Appl. Phys.* **1987**, 62, 716–718.
- (178) Grund, A.; Kaltbeitzel, A.; Mathy, A.; Schwarz, R.; Bubeck, C.; Vermehren, P.; Hanack, M. *J. Phys. Chem.* **1992**, 96, 7450–7454.
- (179) Anderson, H. L.; Martin, S. J.; Bradley, D. D. C. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 655–657.