Third-order nonlinear optical properties of in-backbone substituted oligo(triacetylene) chromophores

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A new approach to tuning the nonlinear optical properties of hybrid oligo(triacetylene) compounds is studied. The method is based on the insertion of a central heterospacer group between two (E)-hex-3-ene-1,5-diyne moieties. A significant increase in the second hyperpolarizability γ is expected if the central spacer fragment is an extended conjugated chromophore. We present a series of molecules with enhanced second hyperpolarizability caused by the presence of highly conjugated spacer groups, which increase the overall π-electron delocalization. Some metal complexes obtained from the coordination of these hybrid oligomers to transition-metal centers have also been investigated and revealed substantial differences in the capacities of the metal centers to act as electronic bridges. Finally, we show that theoretical predictions of the relative differences in the second hyperpolarizabilities of the new spacer compounds are in good agreement with the experimental results. © 2003 Optical Society of America

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1. INTRODUCTION

In recent years, great attention has been devoted to novel organic nonlinear optical materials that show some unique properties that make possible a wide range of applications for achievement of all-optical computing and signal processing.[1–4] In particular, delocalized π-electron systems in organic and organometallic compounds give rise to ultrafast response times and large third-order optical nonlinearities, which, combined with easy processability and low production costs, make these compounds good candidates for use in real devices.[2]

Several methods for improving the third-order susceptibility of a molecule, also called the second hyperpolarizability γ, have been attempted so far in our laboratories[5]: (i) optimization of small chromophores by substituting for them strong electron donor or acceptor groups or both,[6] (ii) increasing the one-dimensional π-electron delocalization over an oligomeric molecular backbone,[7] and (iii) introduction of two-dimensional conjugation paths.[8,9] A new way, through insertion of a heterospacer group into an oligomeric backbone, was presented in a previous paper.[10] This new approach of introducing a spacer group into the conjugation path leads to a series of one-dimensional third-order hybrid nonlinear optical (NLO) chromophores.[10] Some advantages of such (E)-1,2-

diethynylene (DEE) derivatives are good solubility and chemical stability under ambient conditions and laser illumination. To tune and increase the third-order NLO of previously studied oligo(triacetylene) molecules,[10] much effort has been devoted to the improvement of the electronic characteristics of the spacer group (Fig. 1).

The insertion of central heterospacer fragments between two DEE moieties was found to produce only a modest effect on the second hyperpolarizability γ of the resultant hybrid system.[10] In this paper we show how third-order NLO activity can be tuned and significantly improved by insertion of larger π chromophores to extend the conjugation path of the hybrid oligomer into two dimensions (Fig. 1). The existence of different conjugation paths in the spacer unit and the extension of the planar conjugated system both facilitate an increase in the measured NLO effects for new molecules **3–6** (Fig. 1), according to Refs. 8 and 9.

2. EXPERIMENT

In a previous paper our attention was focused on electron-deficient quinoxaline-based heterocycles used as heterospacers.[11] The ends of both DEEs in the hetero-trimeric oligomers are capped with triethylsilyl groups,
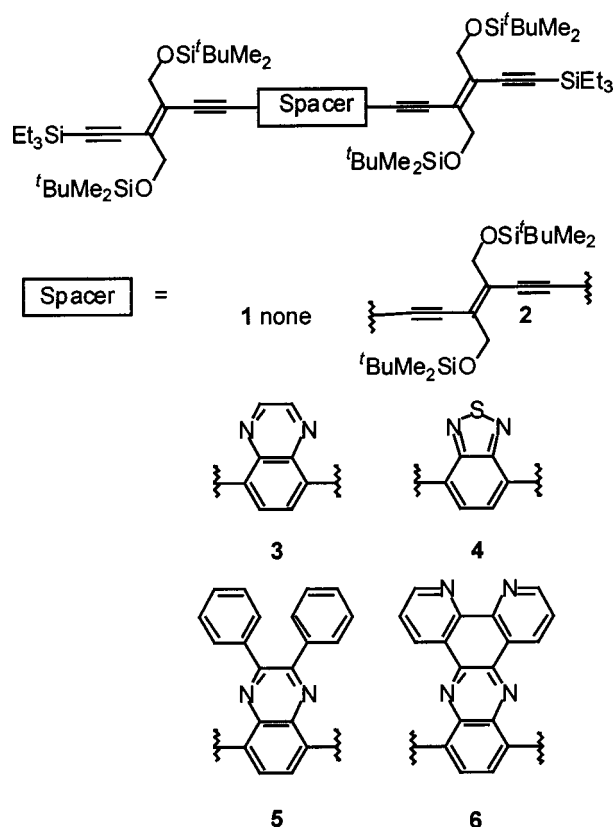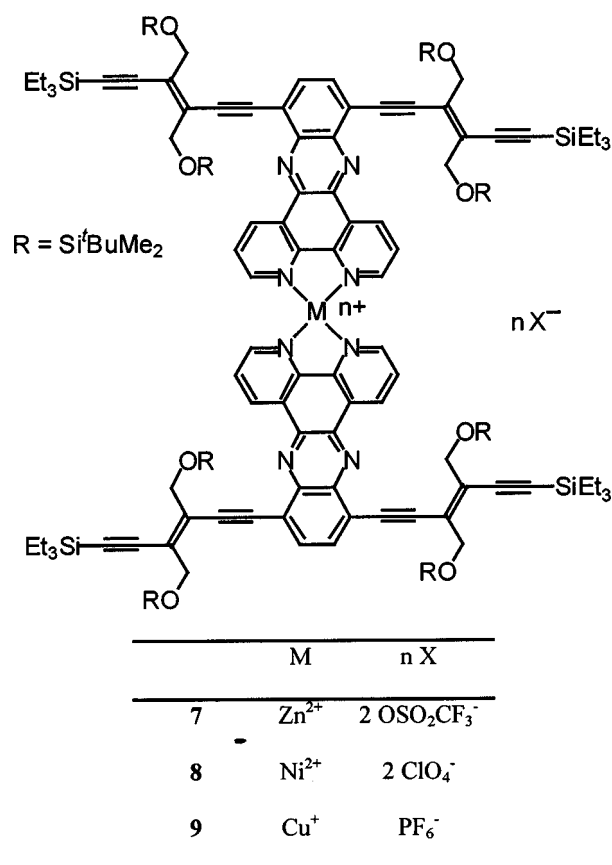
Fig. 1.   DEE homo-oligomers and heterotrimers.

Fig. 2.   Transition-metal complexes: $Zn(\mathbf{6})_2(OSO_2CF_3)_2(\mathbf{7})$; $Ni(\mathbf{6})_2(ClO_4)_2(\mathbf{8})$; $Cu(\mathbf{6})_2PF_6(\mathbf{9})$.

which have negligible electron-donating or accepting power.   In this paper we report on the experimental and theoretical investigation of some of these new oligomeric triacetylene molecules.   The structures of synthesized compounds **3–6** are shown in Fig. 1, together with the structures of DEE homo dimer **1** and homo trimer **2**, which are described in Ref. 12.   Moreover, to study the third-order activity of these new spacer compounds in an organometallic environment we also synthesized some metal complexes with three different metal centers, using molecule **6** as a ligand (Fig. 2).

The second hyperpolarizabilities γ were measured by third-harmonic generation (THG) with a H_2 Raman-shifted Nd:YAG laser (5-ns pulses, 10-Hz repetition rate). The fundamental (1907-nm) and the generated harmonic (635.7-nm) wavelengths lie in the transparency region of the compounds under analysis, resulting in hyperpolariz-abilities that are sufficiently far away from resonance enhancement.   We dissolved the samples in chloroform and measured them at five different concentrations to extract the molecular second hyperpolarizability.   The THG setup was calibrated with a fused-silica plate ($\chi_{fs}^{(3)} = 1.6 \times 10^{-22}\,m^2/V^2 = 1.5 \times 10^{-14}$ e.s.u. at $\lambda = 1907$ nm).[13]

3.   RESULTS AND DISCUSSION

Table 1 lists the measured second hyperpolarizabilities γ for new spacer compounds **3–6**.   For comparison, the nonlinearities for DEE homodimer **1** and homotrimer **2** (Ref. 12) are given as well.

It is noteworthy to examine the spectral features of the new hybrid oligomers, as described in Ref. 11, to analyze the changes in the energy of the first optically excited state of the conjugated molecules and to exclude reso-nance enhancement of the THG process.   The absorption spectra of the quinoxaline-based spacer compounds dis-play a bathochromic shift of the longest-wavelength ab-sorption maximum [$\lambda_{max} = 436$ (molecule **3**), 438 (mol-ecule **4**), 435 (molecule **5**), and 462 (molecule **6**) nm] with respect to homodimer **1** and homotrimer **2**,[12] where the latter shows a greater increase in π-electron delocaliza-tion along the backbone than the former.   The new het-erospacers are much more efficient in facilitating π-electron delocalization along the linearly conjugated oli-gomeric backbone.   This facility can be attributed to the increased extension of their conjugated π systems into two dimensions.   The new hybrid chromophores **3–6** showed an enhanced third-order NLO activity compared to DEE homodimer **1** and homotrimer **2** as a result of the introduction of the heterospacers.   By increasing the ex-tension of the π system of spacers we measured an en-hancement of γ that went from 150×10^{-36} esu for quinoxaline-based chromophore **3** to 220×10^{-36} esu for dipyrido-phenazine-based hybrid oligomer **6** (Table 1). Only spacer compound **3** exhibits a γ value as low as that recorded for DEE homotrimer **2**.   Compound **4** features an enhanced second hyperpolarizability owing to the presence of a benzothiadiazole spacer, which, by its re-duced aromaticity, favors electron delocalization along the conjugated backbone.   The grafting of two benzene rings onto the quinoxaline ring in compound **5** enhances the second hyperpolarizability with a shift of the absorption

Table 1. Comparison of DEE Spacer–DEE Hybrid Oligomers 3–6 and of Metal Complexes 7–9
with Homodimer 1 and Homotrimer 2

Spacer Group Type	Compound	λ_{max} (nm)[a] [ϵ (M^{-1} cm^{-1})]	γ $\times 10^{-36}$ esu[b]	$\times 10^{-48}$ m^5/V^{2b}	$\gamma \times 10^{-36}$ esu Calculated[c]	$\gamma \times 10^{-36}$ esu Corrected[c]
None	**1**	376	45	0.63		
Monomer	**2**	407	150	2.10		
Quinoxaline	**3**	436	150	2.10	327	160
Benzothiadiazole	**4**	[22300] 438	167	2.33	336	164
Diphenylquinoxaline	**5**	[35900] 435	178	2.49	343	167
Dipyridophenazine	**6**	[24100] 462	223	3.12	409	200
$Zn(\mathbf{6})_2(OSO_2CF_3)_2$	**7**	[25800] 471	307	4.29		
$Ni(\mathbf{6})_2(ClO_4)_2$	**8**	[28900] 485	465	6.50		
$Cu(\mathbf{6})_2PF_6$	**9**	[32400] 469 [42500]	494	6.91		

[a] Wavelength of maximal absorption λ_{max}.
[b] Second hyperpolarizabilities $\gamma(-3\omega, \omega, \omega, \omega)$ [reference fused silica, $\chi^{(3)} = 1.6 \times 10^{-22}$ m^2/V^2; experimental error, 10% (Ref. 13)].
[c] γ Values calculated at $\lambda=1907$ nm by the PM3 method before and after the empirical correction.

peak to longer wavelengths.[11] The increased extension of the π-electron conjugation paths strongly influences the third-order NLO activity of the whole molecule. The enforced planarity of the spacer in compound **6**, compared with that of compound **5** with its two vicinal phenyl rings turned out of the quinoxaline plane, further enlarges the nonlinearity with a redshift in the absorption spectrum.

In the whole series of spacer-modified oligo(triacety-lene) compounds, including previously synthesized ones,[10] the new hybrid oligomers **3–6** show the highest second hyperpolarizabilities (γ). This clearly indicates that the insertion of a highly extended two-dimensionally conjugated and planar spacer unit significantly affects the third-order nonlinearity of the oligomer.

Theoretical calculations of the second hyperpolarizability γ were performed on spacer compounds **3–6**. The molecules were geometry optimized, and the second hyperpolarizabilities were calculated by the AM1 and PM3 methods included in the MOPAC computer software package.[14,15] The calculation was performed at the same wavelength of the experimental THG apparatus ($\lambda=1907$ nm). Because there are several approximations of self-consistent field methods, the reliability of the computed values is usually poor,[16] and therefore the theoretical investigations are used only to provide qualitative information. It should be pointed out that there are a number of pitfalls to be considered, including local field effects, an inconsistent choice of conventions in defining the nonlinearities, and dispersion effects caused by experiments conducted at various fundamental frequencies. However, for the series of analogous compounds under consideration, a predictable trend is evident. Thus the theoretical calculations have accurately reproduced the experimental ranking in terms of third-order optical nonlinearity.[8]
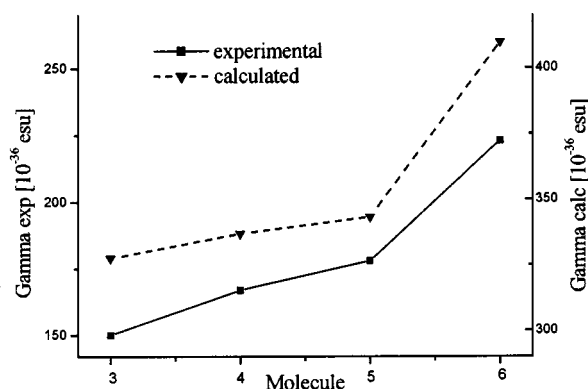

Fig. 3. Comparison of experimental and calculated values of the second hyperpolarizability. Trend after empirical correction for oligomers **3–6** (see text).

In this study, the γ_{PM3} values computed by the PM3 method appeared to be systematically higher than the experimental values by approximately a factor of 2. We used this factor here to empirically correct the computed γ_{PM3} values (Table 1). We made an extensive analysis, using a consistent set of molecules, and a linear fit was produced that shows that the experimental second hyperpolarizability can be obtained from the PM3 results by the transformation $\gamma_{PM3} = 38.9$ e.s.u. $+ 1.8\gamma_{exp}$.[17] To compare the experimental and the computed values, we plot the two trends in Fig. 3, using different scales. Good qualitative agreement is evident and confirms the applicability of theoretical calculations in designing new materials. It could greatly simplify the design of suitable molecules and materials, indicating convincingly the more promising molecules that will probably exhibit higher second hyperpolarizabilities.

To test the potential applications of oligomers **3–6** integrated as guest molecules in an organic material, we estimated the ability of these molecules to exhibit high macroscopic third-order nonlinear optical susceptibility $\chi^{(3)}$ in bulk. Assuming that all the oligomeric rods derived from molecules **3–6** will be organized in a similar way, without any indications about the long-range order of the aggregates, we made the estimation by evaluating the volume of the molecules[18] and consequently the molecular density of the material. The results are given in Table 2.

We can estimate $\chi^{(3)}$ as follows[3]:

$$\chi^{(3)} \propto k \, \gamma N_v ,$$

where k is an unknown factor that depends on local field corrections and the possibility of intermolecular interactions; N_v is the number of molecules per unit volume, and γ is the molecular hyperpolarizability. In Fig. 4 the ratio of the calculated $\chi^{(3)}$ to the $\chi^{(3)}$ of oligomer **3**, called relative $\chi_N^{(3)}$, is shown for comparison. An analysis of the figure indicates that heterotrimers **3** and **6** are the best candidates for achievement of NLO bulk materials.

To explore the potential of transition-metal complexes we modified compound **6** for further NLO investigations. The new metal complexes **7–9** were synthesized by complexation of the bidentate 1,10-phenanthroline-type

Table 2. Estimation of Relative Third-Order Susceptibilities $\chi^{(3)}$ of Compounds 3–6 on Insertion into Bulk Material

Compound	Volume (Å³)[a]	$\chi_N^{(3)}$ (Exp.)[b]	$\chi_N^{(3)}$ (Calc.)[c]
3	916.18	1.00	1.00
4	963.45	1.06	0.97
5	1105.22	0.98	0.86
6	1090.29	1.25	1.05

[a] The Connolly solvent-excluded volume, i.e., the volume contained within the contact surface created when a spherical probe sphere (representing the solvent) is rolled over the geometrically optimized molecular model. 1 Å=0.1 nm.
[b] Normalized $\chi^{(3)}$ obtained by the ratio between experimental γ values and normalized molecular volumes (relative to the volume of the smallest molecule).
[c] Normalized $\chi^{(3)}$ obtained by the ratio of computed γ values to normalized molecular volumes (see Fig. 4).
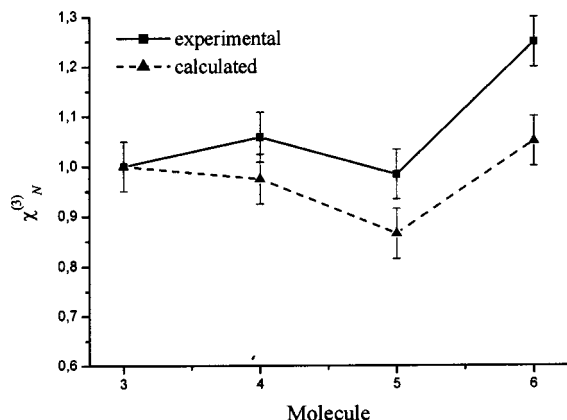
ligand **6** with transition-metal ions Zn^{2+}, Ni^{2+}, and Cu^+.[11] We characterized the complexes by THG to test whether the electronic conjugation can be maintained through the metal center. All the complexes possess tetrahedral coordination geometry, with two molecules **6** per metal center (Fig. 2). The tetrahedral coordination geometry should be favored over a square-planar array for steric reasons: In a tetrahedral complex the two heterotrimer rods stay approximately perpendicular to each other, leaving more space for the bulky $(t\text{-Bu})Me_2SiO$ side chains,[11] although some distortions in the complex geometry often occur, depending on the steric hindrance and electronic nature of the ligands.

The γ values for metal complexes **7–9** correspond to that for the full complex shown in Fig. 2 and would therefore be expected to be twice as large as that of molecule **6**, barring the effects of complexation on the electronic structure.

For metal complexes **7–9**, the spectral absorption characteristics are similar to those of molecule **6** (Ref. 11) and show three bands, at $\lambda=250$–270, 300–360, 430–550 nm, where the molar extinction coefficients are of the same order of magnitude but higher than those measured for ligand **6**. Complexation, in addition, introduces an additional redshift of the longest-wavelength absorption maximum [$\lambda_{max} = 471$ (complex **7**), 485 (complex **8**), and 469 (complex **9**) nm] relative to free ligand **6** and to homodimer **1**, and homotrimer **2** as well.

The complexes that were studied showed improved NLO behavior following the sequence **7**, **8**, **9**. The best performances were produced by the nickel and copper complexes, which showed a second hyperpolarizability γ approximately twice as high as for complex **6**, as expected from the number of molecular units and the tetrahedral or distorted tetrahedral geometry of the complex, avoiding a good conjugation path from one ligand **6** to the other through the metal center. In a closer look, we observed γ values slightly larger than a factor of 2 for Ni^{2+} (complex **8**) and Cu^+ (complex **9**). The NLO activity of zinc complex **7**, however, was significantly less than a factor of 2 of the value measured for molecule **6**. Clearly the electronic communication between the two ligand moieties across the transition-metal ion varies with the nature of the ion.

4. CONCLUSIONS

In conclusion, with this research we have further explored methods of inserting heterospacer functional groups into a molecular backbone to tune the second hyperpolarizability and have extended an earlier study of the modulation of π-electron conjugation of oligo(triacetylene) compounds by insertion of central heterospacer fragments between two DEE units.[10] This approach offers high flexibility for designing new materials with good solubility and high chemical stability, showing that the introduction of electron-deficient quinoxaline-based heterocycles leads to a significant improvement of the second hyperpolarizabilities. We demonstrated that the insertion of large planar extended π-conjugated groups into the backbone of a substituted oligo(triacetylene) system is valuable for modulating the π-electron conjugation and

Fig. 4. Comparison of the experimental and calculated $\chi_N^{(3)}$ trends for oligomers **3–6**.

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consequently the electronic properties of the material. This study of the NLO behavior of three transition-metal complexes showed a slightly enhanced THG behavior on introduction of heterocyclic ligand **6** into the coordination spheres of some of the metal ions considered. This result validates the use of this oligomeric ligand as a potential building block for the preparation of ordered supramolecular nonlinear optical materials. We also showed that compound **6** should be used as a NLO-active module in bulk materials. For example, new NLO polymers could be obtained by introduction of ligand **6** as the repeat unit into a polymer chain, yielding materials with enhanced third-order NLO activity, depending on the bulk molecular packing of the chromophores inside the material.

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