

## Third-order nonlinear optical properties of in-backbone substituted conjugated polymers

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(Received 5 April 2002; accepted for publication 25 July 2002)

We present an alternative approach to tune the third-order nonlinear optical properties of organic molecules by inserting a functional group into the path of the  $\pi$ -electron conjugation instead of at its ends. We show that this scheme has a beneficial influence on the second-order hyperpolarizability for short molecules, but that in two instances where such molecules were polymerized into longer molecules the overall hyperpolarizability is reduced. © 2002 American Institute of Physics. [DOI: 10.1063/1.1507834]

One-dimensionally conjugated oligomers and polymers, with their extended delocalization of  $\pi$  electrons along the molecular backbone, are interesting materials for third-order nonlinear optics. One of the most widely applied strategies to tailor the physical properties of such linearly conjugated chromophores is to insert electron donating and/or accepting groups. In the case of an one-dimensional conjugation, this substitution can only be performed at the two end groups, resulting in a limited freedom to vary the molecular structure. Solutions to circumvent this disadvantage are two-dimensional conjugation<sup>1,2</sup> or substitution of functional groups in the polymer backbone itself. In this work, we explore the second strategy and show the impact of the in-backbone substitution (Fig. 1) on the third-order nonlinear optical properties and the transparency range.

Relationships between the structure and the second-order hyperpolarizability  $\gamma$  of a molecule<sup>3–5</sup> are of prime importance to push the nonlinearities to larger values. Establishing predictive structure-property relationships could lead to materials with a sufficiently large nonlinear refractive index to enable instantaneous all-optical switching and signal processing as, for example, desired in the telecommunication industry.<sup>6</sup>

The strategies to improve the second-order hyperpolarizability  $\gamma$  of a molecule, and consequently the third-order susceptibility  $\chi^{(3)}$  of a material, are not as well developed as in second-order nonlinear optics. Two main approaches can be distinguished: optimization of small chromophores by substituting strong electron donor and acceptor groups and conjugated polymers with an extended delocalization of the  $\pi$  electrons but without donor or acceptor functionalities.

For our investigation of the in-backbone substitution, we chose poly(triacetylene) (PTA) as the basic linearly conju-

gated building block (Fig. 1).<sup>7,8</sup> Although PTA is not the backbone with the best delocalization of the  $\pi$  electrons, the third-order susceptibilities  $\chi^{(3)}$  are comparable to other conjugated polymers when measured outside resonance enhancement. The advantages of PTA are the possibility of selectively substituting the backbone with functional groups, the good solubility, and the chemical stability under ambient conditions and laser illumination.

To evaluate the influence of a functional group in the backbone conjugation, we synthesized molecules with different “spacer” groups (Fig. 2) between two PTA monomers.<sup>9</sup> The other ends of both PTA monomers are capped with trimethylsilyl groups, which have negligible influence on the electron density distribution of the backbone.

Besides the various organic spacer units investigated in this study, we have also considered one organometallic compound. Platinum(II) spacer compound (**i**) (see Table I) is interesting because of the ongoing discussion<sup>10</sup> to which degree conjugation can be maintained through a metal center. In the case of the pyridine (**j**) and pyrazine (**k**) (Table I) derivatives, the nitrogen atom can be protonated by addition of an organic acid. The positive charge influences the electron wave functions of the conjugate backbone and thus changes the second-order hyperpolarizability compared to the unprotonated molecule.

The anthracene-PTA hybrid (**f**) (Table I) shows bright blue-green fluorescence in solution. After several hours of laser illumination, decomposition of the compound is observed when kept in air. For the time period of the characterization experiments, the decomposition is not a problem,

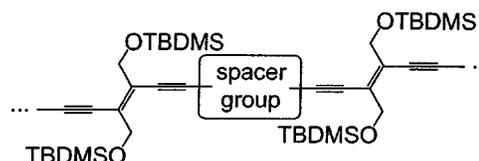


FIG. 1. An attractive method to modulate electron density distribution in conjugated oligomers and polymers is direct incorporation of functional groups (spacers) into the backbone. In this work, the conjugated oligomers are poly(triacetylene)s (PTAs) containing solubility-providing OTBDMS [(*tert*-butyl)dimethylsilyloxy] side chains.

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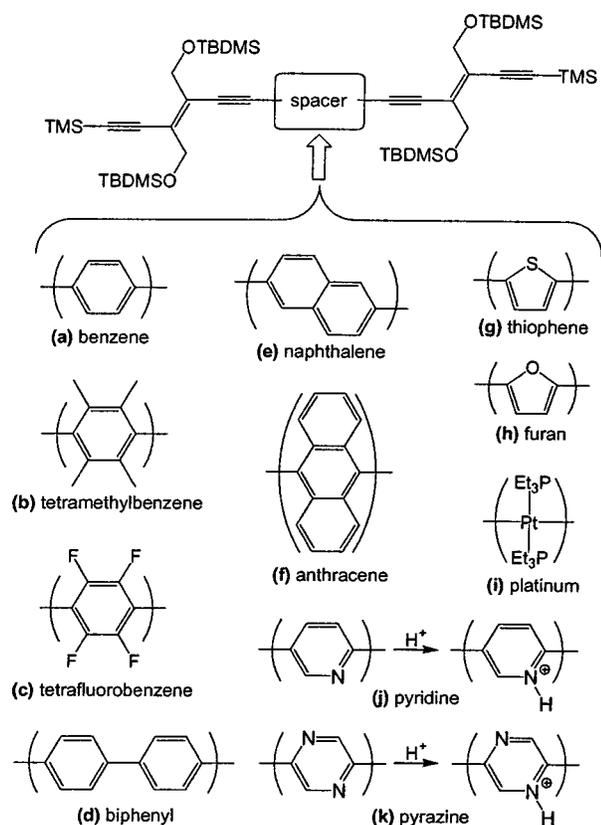


FIG. 2. Molecular structures of the various spacer groups inserted between two monomer units of PTA. The pyridine (i) and pyrazine (k) can be protonated by an organic acid. The TMS end groups denote trimethylsilyl.

but for applications a sealed packaging would be necessary.

The second-order hyperpolarizabilities  $\gamma$  are measured by third-harmonic generation (THG) with a  $H_2$ -Raman shifted Nd:YAG laser (5 ns pulses, 10 Hz repetition rate). The fundamental and the harmonic wavelength of 1907 and 635.7 nm are clearly in the transparency region of the absorption spectra of all studied molecules.<sup>9</sup> Therefore, we can safely assume that the measured hyperpolarizabilities  $\gamma$  are not resonance enhanced. The samples are dissolved in chlo-

TABLE I. Second-order hyperpolarizabilities  $\gamma$  measured by THG at a wavelength of  $\lambda = 1907$  nm. Additionally, the longest-wavelength absorption maxima  $\lambda_{\max}$  are given. The experimental errors of  $\gamma$  are 10%.

Spacer group	$\lambda_{\max}$ (nm)	$\gamma$ ( $10^{-36}$ esu)	$\gamma$ ( $10^{-48}$ m <sup>5</sup> /V <sup>2</sup> )
None (PTA dimer)	376	45	0.63
Pure PTA trimer	407	150	2.12
Benzene (a)	374	54	0.76
Tetramethylbenzene (b)	384	71	1.00
Tetrafluorobenzene (c)	382	120	1.65
Biphenyl (d)	351	100	1.40
Naphthalene (e)	381	150	2.11
Anthracene (f)	495	130	1.79
Thiophene (g)	404	87	1.22
Furan (h)	398	72	1.01
Platinum (i)	342	47	0.65
Pyridine (j)	376	43	0.60
Protonated pyridine (j <sup>+</sup> )	380	37	0.52
Pyrazine (k)	392	98	1.36
Protonated pyrazine (k <sup>+</sup> )	382	73	1.02

roform and measured at various concentrations. The THG setup is calibrated with a fused silica plate ( $\chi_{fs}^{(3)} = 1.6 \times 10^{-22}$  m<sup>2</sup>/V<sup>2</sup> =  $1.15 \times 10^{-14}$  esu at  $\lambda = 1907$  nm).<sup>11</sup>

Table I shows the measured second-order hyperpolarizabilities  $\gamma$  for the various spacer-PTA hybrid oligomers. For reasons of comparison, the nonlinearities of the pure PTA dimer and trimer are also given.<sup>8</sup>

The largest second-order hyperpolarizability  $\gamma$  is measured for the naphthalene-PTA hybrid oligomer (e). Surprisingly, its value of  $\gamma$  is only as good as for the pure PTA trimer. Considering the smaller size of the naphthalene compared to a PTA monomer, the macroscopic nonlinearity  $\chi^{(3)}$  might be bigger than for pure PTA. The longest wavelength absorption maximum  $\lambda_{\max}$  is only slightly redshifted from that of the PTA dimer (Table I), which makes it an interesting candidate for a polymerized sample.

The anthracene derivative (f) shows a redshift of  $\lambda_{\max}$  by more than 100 nm, but the nonlinearity is only modestly enhanced compared to the naphthalene derivative (e) or the pure PTA trimer. In view of the stability concerns mentioned earlier, the anthracene spacer does not seem to be a preferable choice for further investigations.

The PTA derivative with a tetrafluorobenzene (c) spacer group also exhibits a considerably enhanced second-order hyperpolarizability. The nonlinearity is nearly as large as for the anthracene spacer (f), but the absorption spectrum is hardly shifted to the red from the pure PTA dimer. Another interesting aspect related to this structure is that its backbone remains free of any C–H bonds. This can be of importance for the optical transmission in the infrared as the overtones of the C–H vibrations play a significant role. However, to obtain a compound entirely free of disturbing C–H bonds, the side chains of the two PTA monomer units and the terminal silyl moieties would have to be modified as well.

The incorporation of a benzene ring (a) enhances the second-order hyperpolarizability only slightly and also the absorption peak stays more or less at the same wavelength as for the pure PTA dimer. The grafting of four methyl groups (b) on the benzene ring enlarges the nonlinearity further while causing only a minor shift in the absorption spectrum. The addition of another benzene ring leads to the biphenyl spacer molecule (d), for which the second-order hyperpolarizability is considerably increased while at the same time the absorption band is moved to even smaller wavelengths. However, compared to the naphthalene derivative (e), only a 50% enhancement of the  $\gamma$  value is measured for (d).

Surprisingly, insertion of spacers containing electron-density providing S and O atoms such as thiophene (g) and furan (h), leads only to a modest increase of the nonlinearity. The thiophene spacer (g) reduces the  $\gamma$  of the pure PTA dimer in contrast to the pyrazine (k), which shows a larger second-order hyperpolarizability than the other hybrid compounds with the heterocyclic rings thiophene (g) and furan (h).

Protonation of the pyridine (j<sup>+</sup>) with trifluoroacetic acid reduces the nonlinearity only a little, which correlates with the minor shift of  $\lambda_{\max}$ . In the protonated pyridine, the  $\pi$  conjugation circumvents the positively charged nitrogen by passing on the other half of the aromatic ring. The pyrazine exhibits a larger reduction of the second-order hyperpolarizability upon protonation (k<sup>+</sup>) as apparently the positive

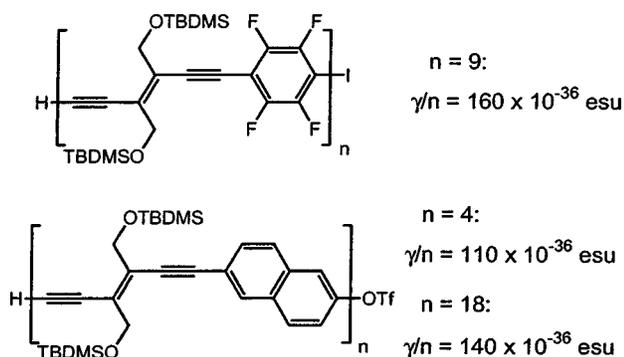


FIG. 3. Structures of the two AB-type polymeric samples and the measured second-order hyperpolarizabilities  $\gamma$ . OTBDMS denotes (*tert*-butyl)dimethylsilyloxy and Tf is trifluoromethanesulfonyl.

charge can disturb both conjugation paths of the ring.

The platinum derivative (**i**) shows more or less the same second-order hyperpolarizability than the pure PTA dimer, but  $\lambda_{\text{max}}$  is shifted significantly to the blue. Normally, the shift of the spectra to shorter wavelengths indicates a reduced conjugation, however, in the present case this blueshift does not seem to influence the nonlinearity. A similar approach with platinum has been pursued for the two-dimensionally conjugated tetraethynylethenes (TEE).<sup>10</sup> The wavelength of maximal absorption did not shift to the red when changing to higher oligomers, and the second-order hyperpolarizability increased only linearly. Based on this experience with Pt-TEE oligomers and the results shown here for hybrid chromophore (**i**), the further exploration of linking monomers by metals does not seem to be promising.

In order to explore the development of the nonlinearities in longer-chain polymers, we chose to further investigate the naphthalene (**e**) and tetrafluorobenzene (**c**) compounds. We prepared AB-type polymers by palladium-catalyzed Sonogashira crosscoupling of suitable hybrid monomers consisting of a PTA monomer connected to a naphthalene or tetrafluorobenzene moiety (Fig. 3).<sup>12</sup> Only relatively short oligomers or polymers could be synthesized. In the tetrafluorobenzene-containing polymer, the 9-mer was the most abundant species. For the naphthalene-containing polymer, both a monodisperse tetramer (4 AB repeat units) as well as a polydisperse sample with a length distribution peaking at 18 monomers (18 AB units) were investigated.

Compared to the pure parent PTA polymer, the AB polymers show lower overall nonlinearities per unit length. Considering the second-order hyperpolarizabilities per number of double and triple bonds  $N$ , a value of  $\gamma/N = 100 \times 10^{-36}$  esu is obtained for the pure PTA.<sup>8</sup> Counting the aromatic rings of naphthalene as 1.5 double bonds each, the value  $\gamma/N = 23 \times 10^{-36}$  esu for the naphthalene-containing AB polymer is about a factor of 4 smaller than for the pure PTA polymer. In the case of the tetrafluorobenzene-containing hybrid polymer, the  $\gamma/N = 36 \times 10^{-36}$  esu is still a factor of about 3 smaller than for pure PTA.

This unfavorable impact of inserting spacers into PTA under formation of AB-type polymers can be understood in the context of the effective conjugation length in the polymer backbone. For various conjugated polymers a superlinear, power-law increase of the second-order hyperpolarizability

versus the number of monomers has been observed.<sup>8</sup> This power law bends over to an only linear increase above a critical conjugation length, which is attributed to the maximal  $\pi$ -electron delocalization distance.

A comparison between the monodisperse tetrameric and the longer, polydisperse samples of the naphthalene-containing hybrid polymer suggests that the effective conjugation length seems to be reached already at 4 monomer units compared to 10 for pure PTA.<sup>8</sup> This earlier saturation of the superlinear increase explains the smaller nonlinearity, although the reason for the smaller effective conjugation length is not yet fully understood. The  $\pi$ -electron localization in naphthalene moieties, which maintain their aromaticity, may hamper  $\pi$ -electron delocalization over many monomer units. Another reason could be distortion from planarity of the backbone caused by the naphthalene spacer group, which would also diminish the strength of the conjugation along the backbone.

In conclusion, we have explored an alternative approach to substitute a linearly conjugated polymer in the backbone itself and evaluated the influence on the third-order nonlinear optical properties. We have determined the impact of various spacer groups between two PTA monomer units on the second-order hyperpolarizabilities of the resulting hybrid oligomers. Significant enhancements of the nonlinearities could be observed with a reduced redshift of the absorption spectra. Based on these measurements, we have investigated two AB-type polymeric samples and found that the overall nonlinearity is smaller than for the corresponding pure PTA polymer. The achievable effective conjugation length seems to be reduced by direct incorporation of aromatic moieties.

The interplay between the delocalization of  $\pi$  electrons along the conjugated backbone and the substitution of the polymer with donor and/or acceptor groups is very critical for optimization of third-order nonlinear optical properties. The incorporation of other spacer groups and a more elaborate synthetic sequences should allow further tailoring of the optical and electronic properties of these materials.

This research was supported by a grant from the ETH Research Council and NCCR "Nanoscale Science."

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<sup>12</sup>Details of the polymerization and full characterization of the AB-type polymers will be described elsewhere.