

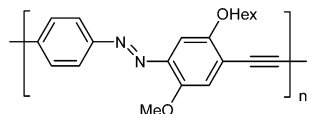
## Second Hyperpolarizability of Ethynyl-Linked Azobenzene Molecular Wires

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A series of oligomers consisting of ethynyl-linked azobenzene units was prepared using Pd-catalyzed cross coupling. The linear and nonlinear optical properties of the oligomers were investigated. The molecular second hyperpolarizability,  $\gamma$ , followed the power law  $\gamma \propto n^{2.12 \pm 0.05}$  ( $n$  is the number of repeat units) for unusually large molecular lengths exceeding 360 conjugated bonds ( $>49$  nm). The exceptional exciton delocalization length is attributed to the rigidity of the conjugated backbone.

Optical switching,<sup>1</sup> optical limiting,<sup>2</sup> 3-D microfabrication, and two-photon microscopy<sup>3</sup> all require materials with a large third-order optical nonlinearity. Conjugated organic materials have long been a focus of this research due to their extended  $\pi$  network and synthetic flexibility. An important structure–function parameter of these materials is the increase in second hyperpolarizability,  $\gamma$ , upon extension of the conjugated backbone. In conjugated oligomers, the evolution of  $\gamma$  is often described using the power law  $\gamma = \gamma_m n^a$ , where  $\gamma_m$  is the second hyperpolarizability of the monomer unit,  $n$  is the number of repeat units, and  $a$  is a constant. The scaling behavior of conjugated systems has been studied experimentally and theoretically.<sup>4</sup> The resultant power laws typically apply to the first several members of an oligomer series. As more repeat units are added, the power law enhancement of  $\gamma$  ( $a > 1$ ) saturates, and  $\gamma/n$  becomes independent of  $n$  ( $a = 1$ ) because of the existence of the proper thermodynamic limit.<sup>4</sup> For one-dimensional molecular wires, the saturation length is typically reached after about 60 conjugated bonds, which correspond to molecular lengths of  $<10$  nm.<sup>5–7</sup>

One-dimensional molecular wires are essentially extended  $\pi$  networks of widely studied chromophores such as stilbene (PPV) or tolane (PPE).<sup>8</sup> In this letter, we describe the effect of incorporating another widely studied chromophore, azobenzene, into extended molecular wires. For conjugated azo oligomers, nonlinear enhancement of  $\gamma$  is observed at unprecedented molecular lengths.



To determine the length dependence of the second hyperpolarizability, a series of oligomers were synthesized using Pd-catalyzed cross coupling.<sup>9</sup> Alkoxy groups have been added to the azobenzene units to improve the solubility of the oligomers.

A complete synthetic scheme is available in the Supporting Information. The resulting oligomers have a rigid conjugated backbone that is essential for nonlinear optical applications.

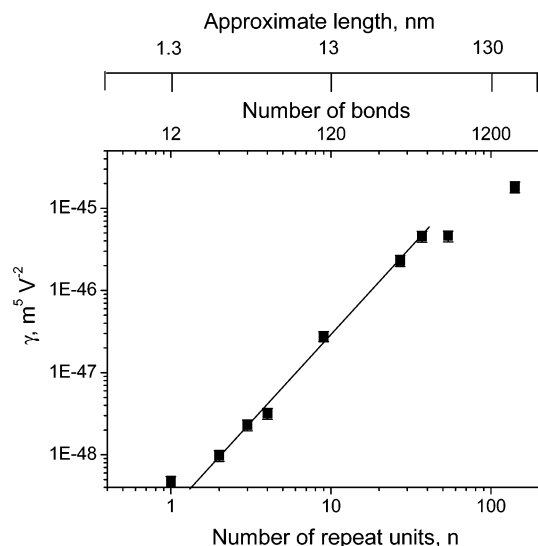
The absorption spectra of the oligomers are shown in Supporting Information Figure S.2A. Absorption spectra indicate strong electronic coupling between azobenzene chromophores. As was previously reported for other poly azo compounds,<sup>10,11</sup> the extinction coefficient increases linearly upon elongation of the conjugated backbone (Figure S.2B). The oligomers also show a bathochromic (red) shift as more repeat units are added. For example,  $\lambda_{\max} = 460$  nm for  $n = 9$ ,  $\lambda_{\max} = 487$  nm for  $n = 27$ , and  $\lambda_{\max} = 496$  nm for  $n = 36$ . The evolution of the bathochromic shift with increasing conjugation length can also be described by a power law; for the azo oligomers,  $\lambda_{\max} \propto n^{0.053 \pm 0.001}$ . Typically,  $\lambda_{\max}$  increases linearly with  $n$ .<sup>12</sup> The smaller exponent for the azo oligomers is a consequence of the unusually small bathochromic shift (36 nm over 27 repeat units). The small bathochromic shift ensures the optical transparency that is required for nonresonant nonlinear optical applications and suggests that the energies of the electronic excited states do not vary significantly over the range of our oligomers.

There is no evidence for saturation of the bathochromatic shift for oligomers  $n < 36$ . This contrasts with a series of phenylethynyl oligomers, where the red shift was found to saturate after approximately 27 repeat units.<sup>13</sup> Due to the close structural similarity between phenylethynyl oligomers and the azo oligomers studied here, the extension of the effective conjugation length most likely results from inclusion of the azo functionality in the conjugated backbone.

The  $\gamma$  values were determined using degenerate four wave mixing (DFWM) at 780 nm with 100 fs laser pulses.<sup>14</sup> The oligomers were studied in tetrahydrofuran (THF) solutions, and neat THF was used as a reference (susceptibility  $\chi^{(3)}_{\text{THF}} = 1.4 \times 10^{-22}$  m<sup>2</sup> V<sup>-2</sup>).<sup>12,14</sup> The second hyperpolarizability length dependence for oligomers  $n = 1–150$  is summarized in Figure 1. The  $\gamma$  values were determined using an analysis described in the Supporting Information. Previously, we showed that, for oligomer  $n = 55$ , the third-order nonlinearity is electronic, and

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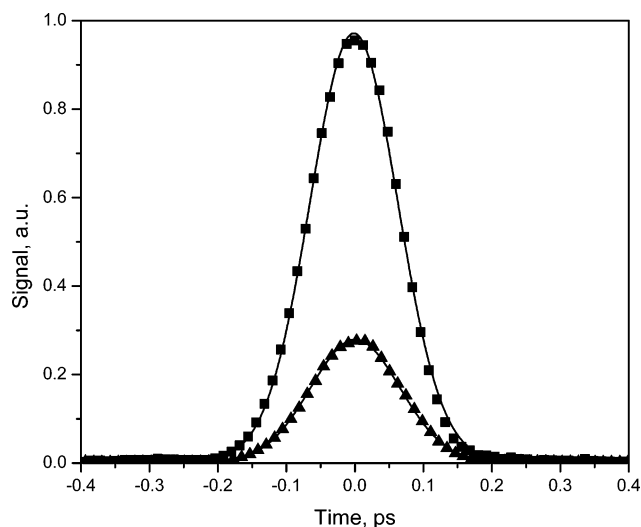
**Figure 1.** Plot showing that the second molecular hyperpolarizability,  $\gamma$ , increases according to the power law  $\gamma \propto n^{2.12 \pm 0.05}$  for azo oligomers  $n = 2-36$ .

we have determined the two-photon absorption coefficient and a nonlinear change in the index of refraction for this compound.<sup>14</sup>

As shown in Figure 1, the hyperpolarizability  $\gamma$  data could be described using a power law of  $\gamma = \gamma_m n^{2.12 \pm 0.05} \text{ m}^5 \text{ V}^{-2}$  for oligomers  $n = 2-36$ . The small  $\gamma$  increase for the monomer  $n = 1$  can be attributed to the end group contribution, while  $n = 55$  and  $n = 150$  oligomers deviate from this power law due to the expected saturation effects.<sup>5-7</sup> The most important finding of this study is the exceptional range of molecular lengths,  $n = 2-36$ , that show a stronger than quadratic increase in  $\gamma$  (and bathochromic absorption shifts). The molecular length in this series of oligomers reaches  $\approx 49 \text{ nm}$ , and the longest oligomer consists of  $>360$  conjugated bonds. This is a significant improvement over the scaling behavior of other molecular wires. For instance, poly(triacetylene) oligomers and oligothiophenyleneethynylenes both showed saturation around 60 conjugated bonds.<sup>5-7</sup> This corresponds to an effective conjugation length of  $7.5 \text{ nm}$  for the poly(triacetylene) series.<sup>5</sup>

The increasing azo oligomer length from  $n = 1$  to  $n = 36$  leads to  $>2000$  times amplification of  $\gamma$ . Calculated per repeat unit, the hyperpolarizability increases  $\approx 27$  times when comparing  $n = 1$  and  $n = 36$  oligomers:  $\gamma_{36}/36 = 127 \times 10^{-49} \text{ m}^5 \text{ V}^{-2}$ , while  $\gamma_1 = 4.7 \times 10^{-49} \text{ m}^5 \text{ V}^{-2}$ . The estimated  $\gamma_m = 2 \times 10^{-49} \text{ m}^5 \text{ V}^{-2}$  value is typical for small organic molecules, including DR1 azo dyes that are often used in photonics applications.<sup>14</sup>

The extraordinarily long effective conjugation length of the azo oligomer could be a result of the rigid structure of the backbone. The oligomers do not have obvious points of conformational flexibility. Cis-trans isomerization around the azo bond of azobenzene moieties is a widely studied process that could potentially have an influence on the  $\pi$  network.<sup>15</sup> We see no evidence of this isomerization in the linear absorption spectra of the oligomers. The same observation was made for other conjugated polymers with azobenzene in the backbone.<sup>16</sup> Phenyl group rotation could also break conjugation. While the phenyl groups can rotate at room temperature in PPE,<sup>17</sup> the influence of the azo group on the threshold for phenyl ring rotation, and hence its impact on conjugation, is not known. Our results suggest that the azo group enhances conjugation through the backbone.



**Figure 2.** DFWM kinetics for  $n = 27$  oligomer solution in THF (concentration  $317 \mu\text{M}$ , ■) and for THF reference (▲). The polarizations of all optical beams used in the experiment were vertical. The solid lines are Gaussian fits to the data with widths (fwhm) equal to  $128 \text{ fs}$ .

The length dependence of the hyperpolarizability,  $\gamma$ , was studied experimentally and theoretically for several organic compounds in order to determine the value of exponent  $a$  and the molecular length at which  $\gamma$  approaches its thermodynamic limit (at the thermodynamic limit, properties begin to scale linearly with an increase in molecular size).<sup>4-7,18</sup> Theoretical studies have shown that the saturation length of the hyperpolarizability is directly related to the exciton coherence size in conjugated oligomers.<sup>4,18</sup> Therefore, the exciton delocalization length in the conjugated ethynyl-linked azobenzene oligomers is exceptionally large, and these oligomers exhibit molecular wire characteristics at molecular lengths up to  $50 \text{ nm}$ . The values of exponent  $a$  predicted in theoretical studies are higher ( $a = 3-5$ ) than those observed for our oligomers.<sup>4,18</sup> However, exponent  $a = 2.12 \pm 0.05$  is similar to values found for other conjugated oligomers:  $a = 2.5$  for polyenes,<sup>7</sup>  $a = 2.46-2.64$  for poly(triacetylenes),<sup>5</sup> and  $a = 2.4$  for oligothiophenyleneethynylenes.<sup>6</sup> The similarity of the exponent  $a$  value found here to those describing other conjugated systems is somewhat unexpected given the much smaller linear absorption bathochromic shifts for the azo oligomers. This result suggests that the extent of electron delocalization could be different in the electronic states that define the linear and nonlinear optical properties of azo oligomers.<sup>19</sup>

Next, we consider if direct excitation into excited states of the oligomers contributes to the nonresonant hyperpolarizability,  $\gamma$ . The DFWM experiments were carried out at different excitation intensities (the optical signals had an expected cubic dependence on the excitation intensity) and at different oligomer concentrations. A representative DFWM kinetics trace for the  $n = 27$  oligomer and the THF reference is shown in Figure 2. The THF reference and oligomer solution data can be fitted with a Gaussian function having the same width (full width at half-magnitude,  $\text{fwhm} = 128 \text{ fs}$ ). In the case of resonant excitation, in which excited states could form by one-photon or two-photon absorption, DFWM kinetics would have a different, slower decaying, temporal profile.<sup>14</sup> The ultrafast, excitation pulse limited, DFWM kinetics indicate that resonant processes do not contribute to the DFWM signals.

No one-photon absorption is expected at  $780 \text{ nm}$  based on the oligomer linear absorption spectra. The DFWM kinetics in Figure 2 indicate that two-photon absorption at  $780 \text{ nm}$  is also

negligible (the same conclusion is obtained from the excitation intensity dependence and concentration dependence studies; see the Supporting Information). Similar results were obtained in open-aperture Z-scan experiments on symmetric azobenzene compounds.<sup>20</sup> Such experiments directly probe two-photon absorption.<sup>20</sup> For symmetric azobenzene compounds, the two-photon cross sections vary by less than 20% at 730–1000 nm.<sup>20</sup>

Negligible two-photon absorption indicates that the symmetries of the oligomer frontier orbitals are determined by the symmetry of the conjugated backbone. The conjugated ethynyl azobenzene backbone has  $C_{2h}$  symmetry, and its electronic states will have either  $g$  or  $u$  symmetry. Two-photon absorption is only allowed between states with the same parity ( $g \rightarrow g$  or  $u \rightarrow u$ ), while one-photon absorption can only occur between states with the opposite symmetry ( $g \rightarrow u$  or  $u \rightarrow g$ ). Therefore, although absorption at 390 nm is strong in the one-photon spectrum (extinction coefficient  $\sim 10^5$  L mol<sup>-1</sup> cm<sup>-1</sup> for  $n = 9$ ), absorption of two 780 nm photons is not allowed by the selection rules. This is consistent with our finding that for all of the oligomers the real component of  $\gamma$ ,  $\text{Re } \gamma$ , is much larger than the imaginary component,  $\text{Im } \gamma$ . As  $\text{Re } \gamma$  reflects nonlinear refraction and  $\text{Im } \gamma$  can be related to two-photon absorption, the azo oligomers studied here primarily have refractive nonlinearities at 780 nm. As such, resonance effects do not contribute significantly to the quadratic enhancement of  $\gamma$ .

In summary, we have found that the rigid conjugated backbone of ethynyl-linked azobenzenes results in an exceptionally long effective conjugation length of more than 36 repeat units (49 nm). This result suggests that the incorporation of azo functional groups and alkynyl linkages into organic optical materials may result in dramatically improved performance in nonlinear optical applications.

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**Supporting Information Available:** Complete synthetic procedures and characterization (NMR, EA, GPC, and UV–

vis) of the oligomers and the details of the DFWM experiment. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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