Supporting Information

Second Hyperpolarizability of Ethynyl Linked Azobenzene Molecular Wires

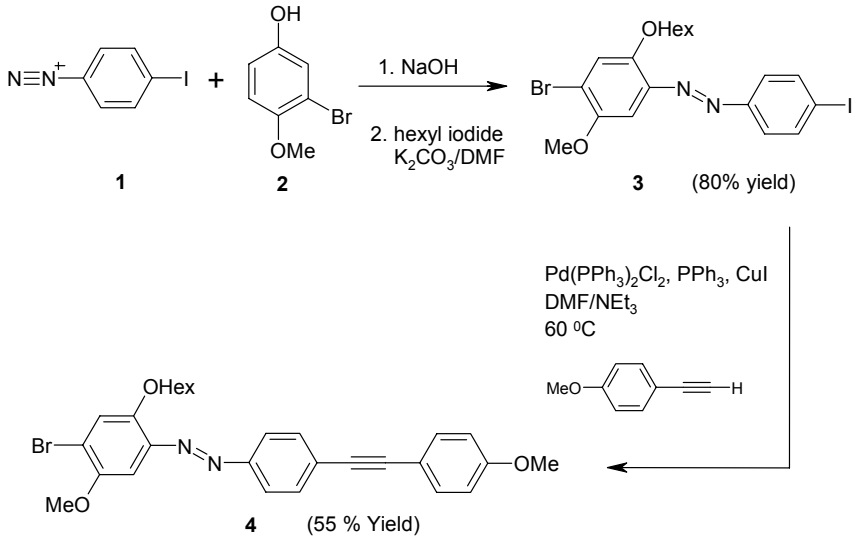
Jonathan L. Humphrey, Kimberly M. Lott, Michael E. Wright,† and Darius Kuciauskas*

Department of Chemistry, Virginia Commonwealth University, Richmond, Virginia 23285-2006

† Chemistry & Materials Division, NAWCWD, Code 4T4220D, China Lake, California 93555

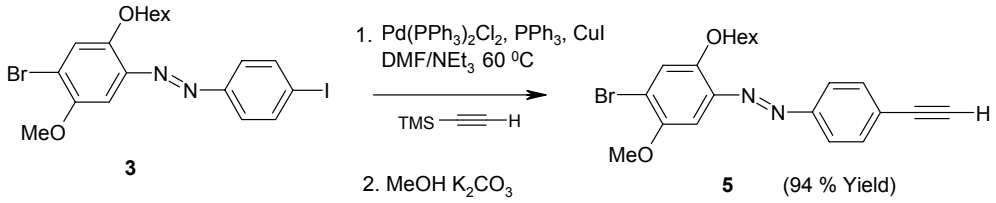
Synthesis of Short (*n*=1-4) Azobenzene Oligomers. Short (*n*=1-4) oligomers were synthesized by controlled chain extension. 3-bromo-4-methoxyphenol (**1**) was reacted with the diazonium salt of 4-iodoaniline (**2**) (Scheme S.1) to provide an azobenzene with an iodine on the less hindered aromatic ring and a bromine at the more substituted aromatic ring. The iodine offers a more reactive site for the coupling reaction to take place. This product, 1-[4-bromo-2-hydroxy-5-methoxyphenylazo]-4-iodobenzene (**3**), was coupled to 4-ethynyl anisole to produce **4** in 55 % yield.

Scheme S.1. The synthesis of **3** and 1-{4-bromo-5-methoxy-2-hexyloxyphenylazo}-4-{4-methoxyphenylethynyl}benzene (**4**)



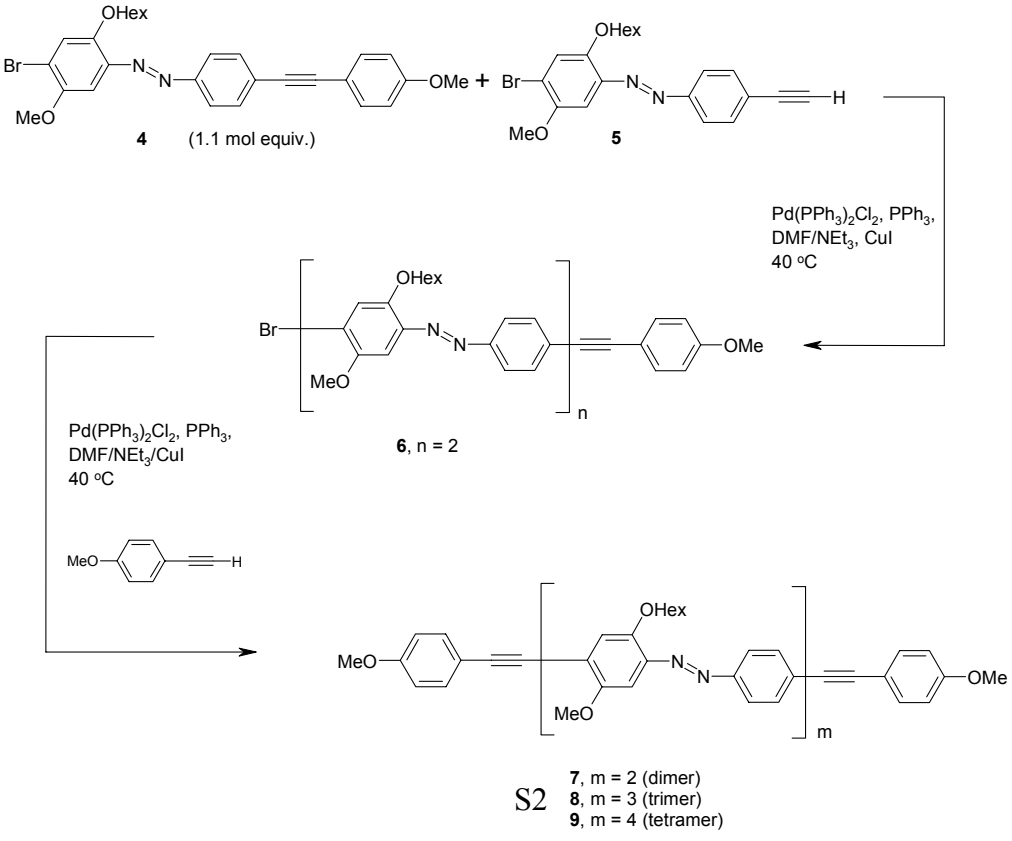
A key intermediate to generating the oligomers was generated via selective reaction of the iodo group in **3** upon treatment with (trimethylsilyl)acetylene, thus affording in high yield the precusor to compound **5**. The trimethylsilyl group was easily removed to afford **5** (Scheme S.2).

Scheme S.2. The Synthesis of {4-bromo-2-hexyloxy-5-methoxyphenylazo}-4-ethynylbenzene (**5**)



Treatment of **5** with 1.1 mol-equiv of **4** was then used to produce dimer **6** by palladium-catalyzed cross coupling (Scheme S.3). The non-end-capped dimer **6** was purified on a silica gel flash column with chloroform as the eluent. Then compound **6** was end-capped with 4-ethynyl anisole to produce dimer **7** that was subjected to final purification by silica gel flash column chromatography using dichloromethane as eluent.

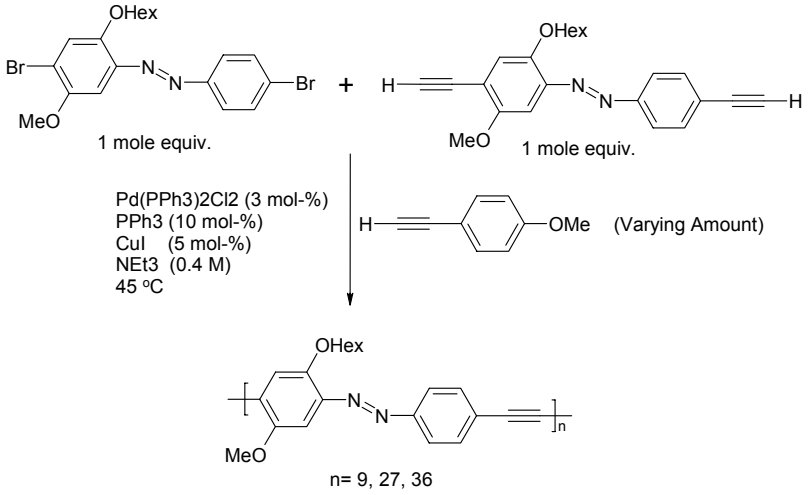
Scheme S.3. Convergent Synthesis of Oligomers **7**-**9**.



The trimer (**8**) was then synthesized by coupling dimer **6** (*n*=2) with 1.0 equivalent of **5**, thus producing a new **6** (*n*=3), and then subsequent end-capping with 4-ethynylanisole affords the desired trimer **8**. Tetramer **9** was prepared by treating **6** (*n*=3, intermediate in the preparation of **8**) with compound **5** followed by an end-capping reaction with 4-ethynylanisole.

Synthesis of Long (*n*=9, 27, 36) Azobenzene Oligomers. Longer oligomers were synthesized by adding increasing amounts of a 4-ethynylanisole end-cap to a palladium cross-coupling polymerization reaction of 4'4-dibromo-2-methoxy-5-hexyloxy-azobenzene and 4,4'-bis(ethynyl)-2-methoxy-5-hexyloxyazobenzene (Scheme S.4).

Scheme S.4. Divergent Synthesis of Larger Azobenzene Oligomers



Increasing the mol-% of endcap produced smaller number average molecular weight (M_n) oligomers. Molecular weights for the oligomers were determined using Gel Permeation Chromatography (GPC) and are reported relative to polystyrene standards.

Detailed Experimental Procedures and Data

General Methods. All manipulations of compounds and solvents were carried out using standard Schlenk techniques. Solvents were degassed and purified by distillation under nitrogen

from standard drying agents. Infrared spectra were measured with Perkin Elmer 1750 FT-IR spectrometer, ^{1}H NMR and ^{13}C NMR measurements were performed using Bruker AC-200 MHz, Varian Mercury 300 MHz, or Varian Inova 400 MHz spectrometers. ^{1}H NMR and ^{13}C NMR chemical shifts are reported versus the respective solvent residue peak (Solvent, ^{1}H, ^{13}C: $CDCl_3$, δ 7.25 ppm, δ 76.9 ppm; DMSO-d_6, δ 2.62 ppm, δ 36.9 ppm). The organic reagents were purchased from Aldrich Chemical Co. and used as received.

Preparation of 4-{4-bromo-2-hydroxy-5-methoxyphenylazo}-1-iodobenzene. To prepare the diazonium salt, 4-iodoaniline (4.95 g, 23.0 mmol) was dissolved in HCl (5.5 mL conc. HCl in 35 mL water). The solution was cooled in an ice bath, and 7 mL of an aqueous solution of $NaNO_2$ (1.70 g, 24.6 mmol) was slowly added. For the coupling reaction, 3-bromo-4-methoxyphenol (4.59 g, 23.0 mmol) was dissolved in 10% NaOH (100 mL). The solution was cooled in an ice bath and the diazonium salt solution was added dropwise. After stirring at 0 °C for 2 h the mixture was acidified with HCl (37% aqueous) and the precipitate was collected by vacuum filtration. The crude product was purified by column chromatography (silica gel, CH_2Cl_2) and after removal of solvent afforded **3** as a dark orange solid (7.82 g, 79%). ^{1}H NMR ($CDCl_3$): δ 7.80 (d, 2H), 7.72 (d, 2H), 7.41 (s, 1H), 7.29 (s, 1H), 3.96 (s, 3H).

Preparation of {4-bromo-2-hexyloxy-5-methoxyphenylazo}-4-iodobenzene (3). A DMF (40 mL) solution containing 4-bromo-4'-iodo-2-hydroxy-5-methoxyoxyazobenzene (7.82 g, 18.0 mmol), hexyl iodide (2.65 mL, 18.0 mmol), and K_2CO_3 (7.46 g, 54.0 mmol) was heated to 40 ^{o}C. After 12 h the reaction was cooled to ambient temperature and diluted with ether (75 mL). The organic layer was washed with water (100 mL), saturated NH_4Cl (100 mL), dried over $MgSO_4$, and concentrated to dryness. The compound was triturated with cold pentane to afford bright red needles (8.92 g, 75%). ^{1}H NMR ($CDCl_3$): δ 7.84 (d, J=9 Hz, 2H), 7.67 (d, J= 8.7 Hz,

2H), 7.34 (s, 1H), 7.32 (s, 1H), 4.13 (t, J= 5.1 Hz, 2H), 3.92 (s, 3H), 1.84 (m), 1.62 (m), 1.36 (m), 0.91 (t, J= 5.1 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$): δ 152.4, 152.1, 141.7, 138.6, 124.9, 120.8, 116.9, 116.8, 99.3, 97.9, 71.3, 56.9, 31.8, 29.5, 25.9, 22.9, 14.3.

Prepartion of 4-{4-bromo-2-hexyloxy-5-methoxyphenylazo}-1-(4-methoxyphenylethynyl)benzene (4). A DMF/Et_3N (10 mL/ 2 mL) solution containing **3** (1.34 g, 2.6 mmol), 4-ethynylanisole (340 mg, 2.5 mmol), $Pd(PPh_3)_2Cl_2$ (55 mg, 0.08 mmol), PPh_3 (68 mg, 0.26 mmol), and CuI (25 mg, 0.08 mmol) was heated to 50 ^oC for 5 h with stirring. The mixture was cooled to ambient temperature and then diluted with ether (50 mL). The organic layer was washed with water (75 mL x 3), dried over $MgSO_4$, and then concentrated to dryness. Purification by column chromatography (silica gel, 50:50, hexanes:CH_2Cl_2) and then removal of solvents afforded **4** as a dark red solid (1.36 g, 47%). ^1H NMR ($CDCl_3$):δ 7.92 (d, J= 6.3 Hz, 2H), 7.63 (d, J= 6.3 Hz, 2H), 7.49 (d, J= 6.9 Hz, 2H), 7.35 (s, 1H), 7.34 (s, 1H), 6.9 (d, J= 6.9 Hz, 2H), 4.14 (t, J= 5.1 Hz, 2H), 3.92 (s, 3H), 3.83 (s, 3H), 1.89 (m), 1.51 (m), 1.39 (m), 0.91 (t, J= 5.1 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$): δ 160.1, 152.1, 150.8, 142.1, 133.4, 132.4, 131.5, 131.0, 130.9, 126.6, 123.4, 123.1, 120.9, 117.9, 116.5, 115.2, 114.3, 113.9, 99.4, 88.4, 71.5, 56.9, 55.6, 31.8, 29.5, 25.9, 22.8, 14.3.

Preparation of {4-bromo-2-hexyloxy-5-methoxyphenylazo}-4-ethynylbenzene (5). A DMF/Et_3N (16 mL/ 2 mL) solution containing **3** (1.92 g, 3.7 mmol), trimethylsilylacetylene (0.52 mL, 3.7 mmol), $Pd(PPh_3)_2Cl_2$ (78 mg, 0.11 mmol), PPh_3 (97 mg, 0.37 mmol), CuI (35 mg, 0.18 mmol) was heated to 50 ^oC with stirring for a period of 5 h. The reaction was cooled to ambient temperature and diluted with ether (75 mL). The organic layer was washed with water (75 mL x 3), dried with $MgSO_4$, and then concentrated to dryness. Purification by column chromatography (silica gel, hexanes:CH_2Cl_2, 1:1, v:v) afforded the TMS-protected product as a

dark red solid (1.50 g, 83 %). ^{1}H NMR ($CDCl_3$): δ 7.87 (d, 2H), 7.60 (d, 2H), 7.34 (s, 1H), 7.32 (s, 1H), 4.16 (t, J= 6.6 Hz, 2H), 3.92 (s, 3H), 1.87 (m), 1.60 (m), 1.35 (m), 0.91 (t, J= 6.9 Hz, 3H), 0.28 (s, 9H). This entire sample was dissolved in CH_3OH/H_2O (50 mL/ 5 mL) and then with stirring at ambient temperature solid K_2CO_3 (1.28 g, 9.3 mmol) was added over a 5 min period. After 12 h of reaction the mixture was diluted with ether (75 mL), washed with H_2O (100 mL x 2), dried over $MgSO_4$, and then concentrated to dryness. The compound was purified by column chromatography (silica gel, 7:93, ethyl acetate:hexanes, v:v) to yield **5** as a red solid (1.2 g, 94%). ^{1}H NMR ($CDCl_3$): δ 7.86 (d, J= 9.0 Hz, 2H), 7.62 (d, J= 8.4 Hz, 2H), 7.34 (s, 1H), 7.31 (s, 1H), 4.12 (t, J= 6.3 Hz, 2H), 3.91 (s, 3H), 3.22 (s, 1H), 1.84 (m), 1.46 (m), 1.34 (m), 0.89 (t, J= 6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 152.7, 152.1, 150.8, 141.9, 133.2, 124.8, 123.2, 120.9, 116.9, 99.29, 83.6, 79.8, 71.8, 71.4, 56.9, 31.8, 29.5, 25.9, 22.9, 14.3.

Preparation of dimer 7. A DMF/Et_3N (4:1) solution containing **5** (0.10 g, 0.2 mmol), **4** (0.115 g, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (4.0 mg, 0.005 mmol), PPh_3 (5.0 mg, 0.02 mmol), and CuI (2.0 mg, 0.015 mmol) was heated to 45 ^{o}C with stirring for a period of 3.5 h. The mixture was diluted with ether (50 mL), washed with water (3 x 100 mL), dried with Na_2SO_4, and concentrated to dryness. Product **6** was subjected to a flash column chromatography (silica gel, $CHCl_3$) and the solvents removed. This product was then stirred in a solution of Et_3N (5 mL), $Pd(PPh_3)_2Cl_2$ (4 mg, 0.005 mmol), CuI (2 mg, 0.015 mmol), PPh_3 (5 mg, 0.02 mg), and 4-ethynyl anisole (30 mg, 0.2 mmol) was brought to reflux. After 4 h the solution was cooled to ambient temperature and diluted with ether (50 mL), washed with water (3 x 100 mL), dried with Na_2SO_4 and concentrated to dryness. Compound **7** was purified by a flash column chromatography (silica gel, CH_2Cl_2) to yield a dark red solid. ^{1}H NMR ($CDCl_3$): δ ^{1}H NMR ($CDCl_3$): δ 7.92 (d, J= 3.3, 2H), 7.91 (d, J= 3.3 Hz, 2H), 7.68 (d, J= 8.6 Hz, 2H), 7.64 (d, J= 9Hz,

2H), 7.52 (d, J= 3Hz, 4H), 7.35 (s, 1H), 7.34 (s, 1H), 7.33 (s, 1H), 7.33 (s, 1H), 6.92 (d, J= 3Hz, 4H), 4.15 (m, 4H), 3.93 (s, 3H), 3.92 (s, 3H), 3.85 (s, 3H), 1.89 (m, 4H), 1.53 (m, 4H), 1.37 (m, 8H), 0.92 (m, 6H).

Preparation of oligomers 8 and 9. In a similar manner to above compound **6** is treated with **5** as the ethynyl reagent. This product can be end-capped with the 4-ethynylanisole or used again in the coupling reaction with **5** to afford the tetrameric compound (minus the endcap). In each case the trimer and tetramer is end-capped using a DMF/Et_3N (4:1) solution containing the oligmer and 4-phenylethynylanisole. Reaction time and workup of the reactions were similar to **7** above.

Oligomer **8:** ^{1}H NMR ($CDCl_3$): δ 7.94 (d, J= 9.3 Hz, 6H), 7.67 (d, J= 8.1 Hz, 6H), 7.50 (d, J= 6.6 Hz, 4H), 7.32 (s, 3H), 7.27 (s, 3H), 6.89 (d, J= 6.3 Hz, 4H), 4.18 (t, J= 9.3 Hz, 6H), 3.97 (s, 9H), 3.91 (s, 9H), 1.89 (m, 6H), 1.52 (m, 3H), 1.36 (m, 15H), 0.93 (t, J= 7.5 Hz, 9H).

Oligomer **9**: ^{1}H NMR ($CDCl_3$): δ 7.94 (m, 8H), 7.64 (m, 4H), 7.51 (m, 8H), 7.37 (s, 4H), 7.31 (s, 4H), 6.90 (m, 4H), 4.17 (m, 8H), 3.96 (s, 12H), 3.89 (s, 6H), 1.89 (m), 1.65 (m), 1.43 (m), 0.919 (m, 12 H).

In-situ oligomerization of {4-bromo-2-methoxy-5-hexyloxyphenylazo}-4-bromobenzene and {4-ethynyl-2-methoxy-5-hexyloxyphenylazo}-4-ethynylbenzene. A triethylamine (0.4 M) solution containing {4-bromo-2-methoxy-5-hexyloxyphenylazo}-4-bromobenzene and {4-ethynyl-2-methoxy-5-hexyloxyphenylazo}-4-ethynylbenzene in a one:one molar ratio, $Pd(PPh_3)_2Cl_2$ (3 mol-%), CuI (5 mol-%), PPh_3 (10 mol-%), and varying amounts (10-20 mol-%) of 4-ethynyl anisole were heated to 60 ^oC. After the reaction was complete, the mixture was cooled to ambient temperature, diluted with ether (75 mL), washed with water (100 mL x 2), saturated NH_4Cl (100 mL), dried with $MgSO_4$ and concentrated to dryness. The higher

molecular weight oligomers were precipitated into cold CH_2Cl_2 (100 mL). Additional purification was done using flash column chromatography (silica gel, 5:95, ethyl acetate:hexanes) if required.

Gel Permeation Chromatography (GPC). GPC data was collected on a Hewlett Packard 1100 HPLC system employing a PL size-exclusion column (300 x 7.5 mm, 5μ particle size) and polystyrene standards. The GPC analysis of the azobenzene oligomers is shown in Figure S.1. (GPC data for oligomer *n*=55 was reported previously.[1]) The elution time decrease with a shortening of the oligomer.

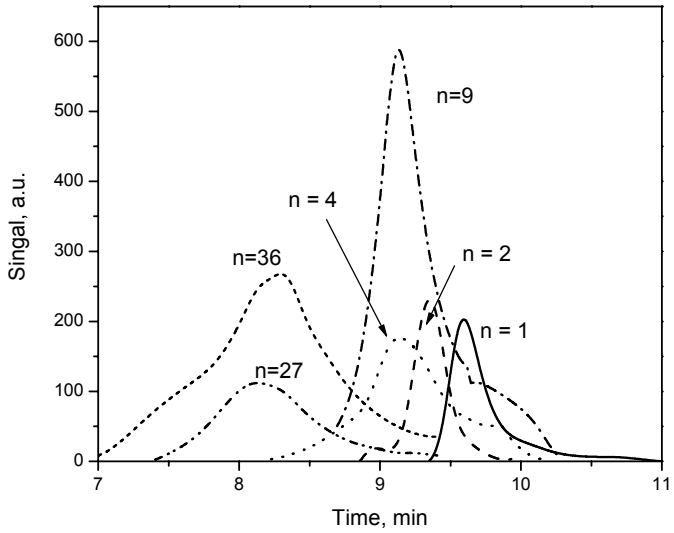


Figure S.1. GPC traces of the azobenzene oligomers.

UV/vis Spectroscopy. UV-vis spectra were measured with a HP-8452A spectrometer. All solutions were dissolved in THF and measured in a 1 cm pathlength quartz cuvette. The spectra and molar extinction coefficients of the oligomers *n* = 4, 9, 26, 39 are shown in Figure S.2A. Figure S.2B summarizes the increase in extinction coefficients and absorption bathochromic shifts with oligomer lengthening. The solid lines in Figure S.2B show the least square fitting obtained using the power laws $\varepsilon \propto n^{1.0\pm 0.1}$ for the extinction coefficients and $E_{max} \propto$

$n^{0.053\pm0.001}$ for the absorption bathochromic shifts (Energy E_{max} corresponds to the absorption band maximum).

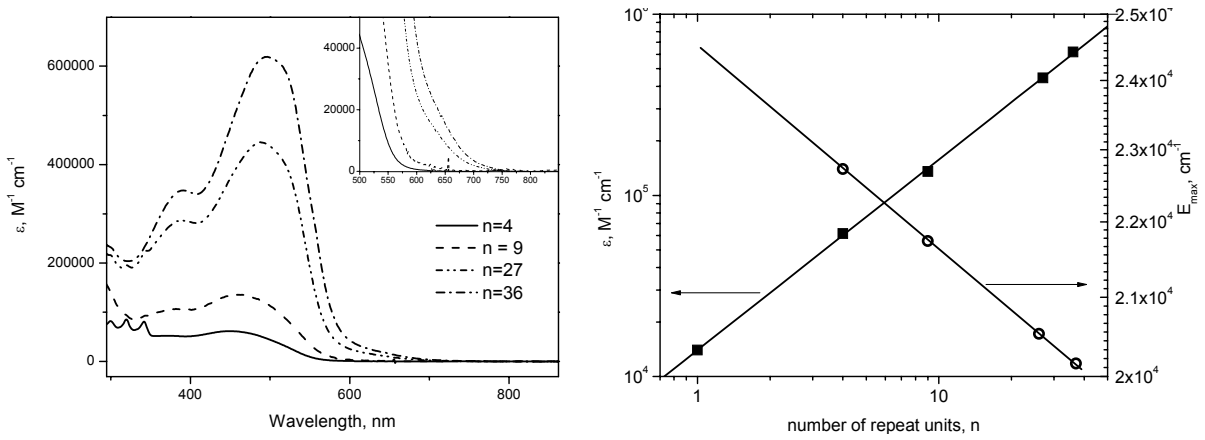


Figure S.2. A: UV/vis spectra and linear extinction coefficients for oligomers *n*=4 (—), *n*=9 (- -), *n*=27 (-··-), and *n*=36 (···). **B**: Molar extinction coefficient, ε, and E_{max} dependence on the oligomer length. Solid lines show fitting results.

Degenerate Four Wave Mixing (DFWM). The DFWM setup was described previously.[1] Each oligomer sample was dissolved in THF, centrifuged at 5000 rpms for five minutes, filtered through a 0.5 μm PTFE filter, and transferred to a 1 mm path length cell. Solutions were magnetically stirred. Due to varying solubilities, different concentration ranges were measured for each oligomer. The tetramer and nonamer solutions were several mM, for *n*=27, the concentration was hundreds of μM, and *n*=36 was run at less than 100 μM.

The intensity dependence of the DFWM signal was determined prior to kinetics measurements. The expected cubic dependence was observed for all samples (Figure S.3). All kinetics runs were performed between 0.20 I_{max} and 0.25 I_{max} (Figure S.4). This corresponds to an excitation intensity of 12.6 GW/cm^2 (20 μJ and 100 fs laser pulses overlapped in an area of 1.13 mm^2).

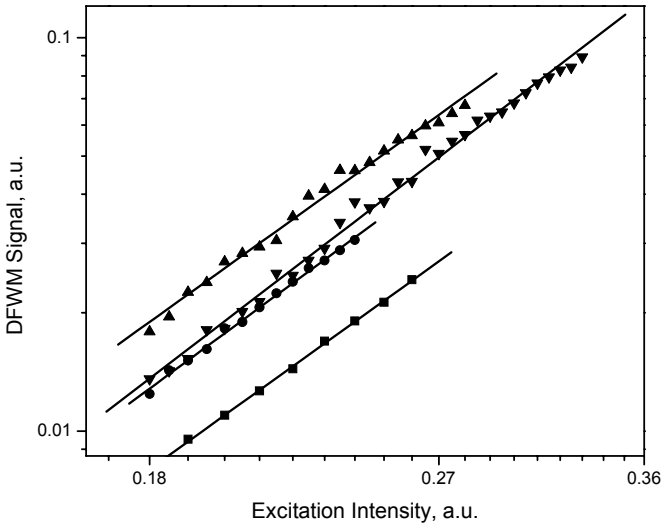


Figure S.3. Intensity dependence of oligomers n = 9 (2 mM, ●), n = 27 (317 μM, ▲), n = 36 (70.5 μM, ▼), and THF (■). All lines are fit to the intensity dependence $I_{signal} \propto I_{excitation}^{3.0\pm0.1}$ (slope 3.0 ± 0.1).

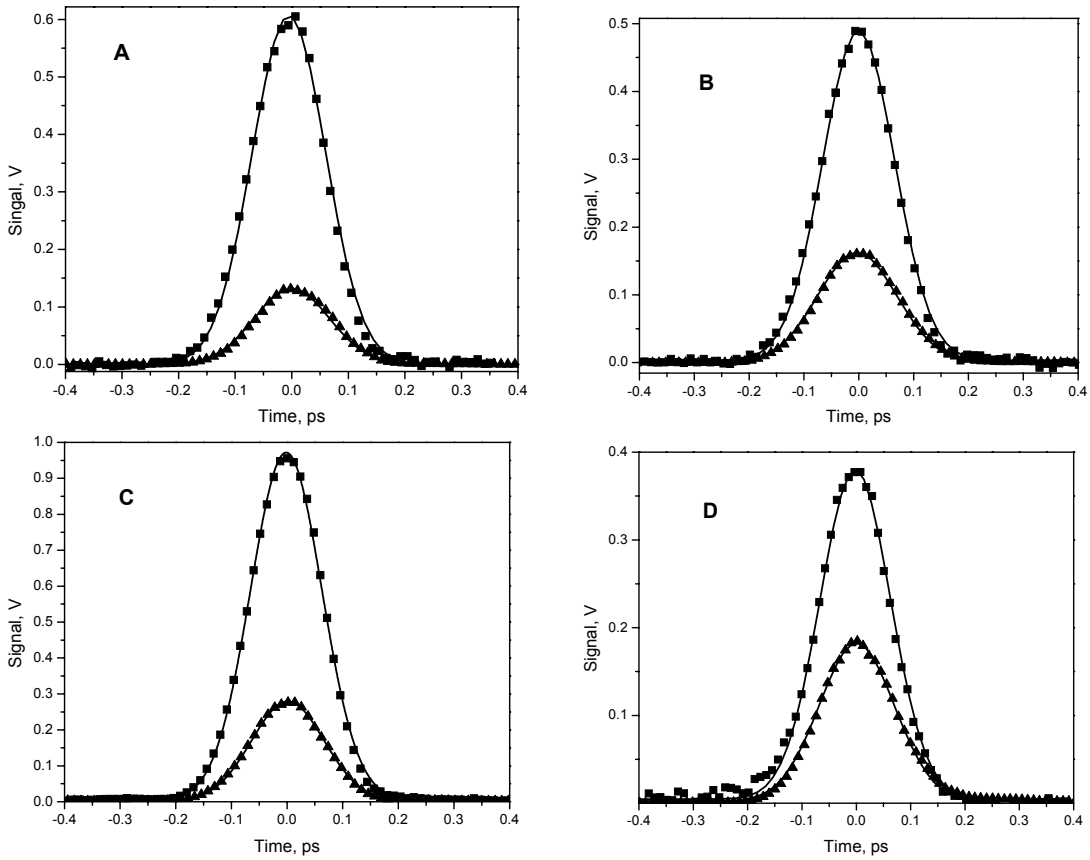


Figure S.4. Typical DFWM signals for n=4 (A, ■, 5.6 mM), n=9 (B, ■, 2 mM), n=27 (C, ■,317 μM), n=36 (D, ■, 70.5 μM), and a THF reference for each experiment (▲). The solid lines are Gaussian fits to the data with a width (FWHM) of 130 fs.

Representative DFWM data for oligomers n = 4, 9, 27, 36 are shown in Figure S.4. The intensity of DFWM signals reflect solution third order nonlinear susceptibility, $\chi^{(3)}_{solution}$. To determine oligomer second hyperpolarizability, γ, we used a literature method.[2] Briefly, a comparison of solution and solvent $\chi^{(3)}$ yields

$$\left|\chi^{(3)}_{solution}\right| = \sqrt{\frac{I_{solution}}{I_{THF}}} \times \chi^{(3)}_{THF} \qquad (1)$$

where $I_{solution}$ and I_{THF} are DFWM signals measured for solution and THF reference. This $\left|\chi^{(3)}_{solution}\right|$ value is used in equation (2) to find |γ|

$$\left|\gamma\right| = \frac{\left|\chi^{(3)}_{Solution}\right| - \chi^{(3)}_{THF}}{Nf^4} \qquad (2)$$

where N is the number molecular density (measured in molecules per cm^3), $f = (n^2 + 2)/3$ (n is refractive index, n = 1.407 for THF), and $\chi^{(3)}_{THF} = 1.4\times10^{-22}$ m^2 V^{-2}.[1,3]

To confirm this approach, $\left|\chi^{(3)}_{solution}\right|$ concentration dependence was measured and analyzed using equation (3)

$$\left|\chi^{(3)}_{solution}\right| = \left(\left|f^4 N_{solute}\,\mathrm{Re}\,\gamma_{solute} + \chi^{(3)}_{solvent}\right|^2 + \left|f^4 N_{solute}\,\mathrm{Im}\,\gamma_{solute}\right|^2\right)^{1/2} \qquad (3)$$

The representative concentration dependence data for the n = 27 oligomer is shown in Figure S.5. Nonlinear least squares fitting using equation (3) yields γ = (2.4±0.2)×10^{-46} m^5V^{-2} and Im γ = 0.0±0.0 m^5V^{-2}; the result is in good agreement with the values obtained using Eqs. (1) and (2) ($|\gamma| = (2.31\pm0.19)\times10^{-46}$ m^5V^{-2}).

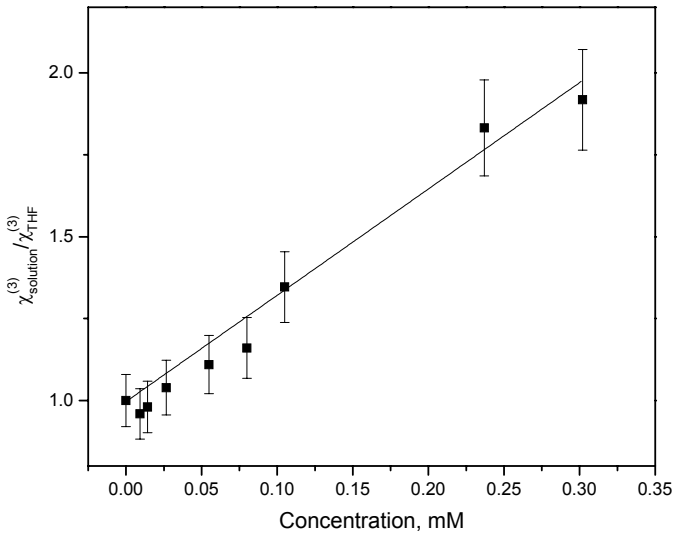


Figure S.5. Nonlinear susceptibility $\chi^{(3)}$ concentration dependence for oligomer *n*=27 (THF solution). The line is a fit to equation (3) with Re $\gamma = 2.4\times10^{-46}$ m^5V^{-2} and Im $\gamma = 0$ m^5V^{-2}.

The same procedure was applied to the other oligomers in order to determine the second hyperpolarizability, γ, values shown in Figure 1.

References

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3. Slepkov, A. D.; Hegmann, F. A.; Eisler, S.; Elliott, E.; Tykwinski, R. R., *J. Chem. Phys.* **2004**, *120*, 6807-6810.