

# Synthesis and Third-Order Nonlinear Optical Properties of End-Functionalized Oligo-Phenylenevinylenes

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Novel homologues series of the highly soluble and coplanar oligo-phenylenevinylenes (OPV), containing up to eight phenyl rings symmetrically end-functionalized with multiple polyalkyleneoxy substituents (OPV(*n*)-OR), and containing up to six phenyl rings, asymmetrically end-functionalized with polyalkyleneoxy and alkylsulfonyl substituents (OPV(*n*)-ORSO), were synthesized for structure-third-order optical nonlinearities investigation. The theoretical molecular nonlinearities,  $\gamma_{\text{calc}}$  at zero frequency calculated by the Finite Field method in MOPAC6 and the time-dependent coupled perturbed Hartree–Fock method within the MOPAC93 package showed a similar trend of the increase with an extension of chain length. However, the predicted  $\gamma_{\text{calc}}$  differences between the symmetrically and asymmetrically disubstituted OPVs are relatively minor. The real part ( $\gamma_{\text{real}}$ ) and the imaginary part ( $\gamma_{\text{imag}}$ ) of the molecular nonlinearities of the newly synthesized OPVs were determined by the closed- and open-aperture Z-scan technique at 800 nm with 100-fs laser pulses in two different solvents. It is evidenced that solvent effect plays an important role in determining third-order nonlinearities of molecules in solution. Although the absorption behavior of these OPVs is very similar in chloroform and tetrahydrofuran (THF), the sign reversal of  $\gamma_{\text{real}}$  from positive to negative appears earlier in chloroform than in THF. The  $\gamma$  enhancement due to asymmetric substitution in lower homologues of these oligomers is significant; however, such contribution becomes less pronounced in the higher homologues. In addition, the asymmetrically disubstituted OPVs show a faster convergence of  $|\gamma|$  than the symmetrically disubstituted series. A very large  $|\gamma|$  value, up to  $2.5 \times 10^{-32}$  esu, was obtained in the symmetrically disubstituted OPVs.

## Introduction

The promise of the nonlinear optical (NLO) materials for optoelectronic and photonic applications has drawn considerable research activity in the past decades.<sup>1,2</sup> One of the attractive applications of third-order NLO materials is all-optical signal processing or switching.<sup>3</sup> Organic materials are considered as one of the important classes of third-order NLO materials because of the ultrafast response, ease of processing and fabrication to waveguide structures, and high optical damage threshold. However, design of organic materials with large and potentially useful third-order optical nonlinearities presents a great challenge for the scientific communities as the third-order NLO properties vary

considerably with various molecular/chain structures as well as the type of functional substituents attached on them.<sup>4</sup>

Poly(phenylenevinylene) (PPV) has been shown to be one of the most promising  $\pi$ -conjugated polymeric materials for third-order nonlinear optics.<sup>5,6</sup> A large nonlinearity is obtainable in PPV; however, linear and nonlinear optical losses in the polysulfonium precursor route PPV are an obstacle in using this material for waveguide applications. Films of PPV are characterized by the poor structural perfection and the high polydispersity, severely affecting their linear and nonlinear optical properties.<sup>7,8</sup> Soluble derivatives of PPV are being investigated, and some of them have been found promising as third-order NLO materials.<sup>9,10</sup> It is of great

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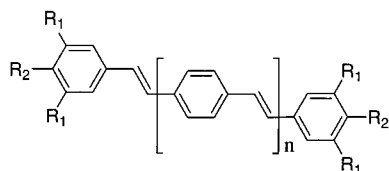
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interest to identify or understand the structure–property relationship of the well-defined model oligomeric materials, such as soluble oligo-phenylenevinylenes (OPV). This knowledge is critical for a rational design of new third-order NLO materials based on both low molecular weight molecules and on polymeric chains.<sup>4</sup>

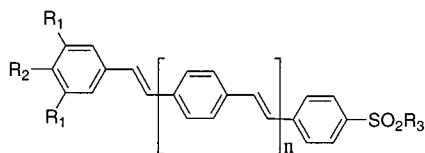
We herein report on the synthesis of the novel symmetrically and asymmetrically end-functionalized coplanar OPVs containing up to eight phenyl rings and the results of an investigation of structure–third-order-NLO-properties relationship. In addition, the semiempirical calculations were used to calculate the molecular hyperpolarizabilities,  $\gamma$ , in order to understand and correlate the experimental results. Because of rigidity and planarity of the  $\pi$ -conjugated phenylenevinylene units, unsubstituted PPV and higher homologues of related OPVs are highly insoluble. To preserve their unique characteristics (or functional properties) and alleviate the solubility problem, we have previously synthesized a series of highly light-emitting coplanar OPVs containing up to six phenyl rings bearing solubilizing dimethoxy-polyalkyleneoxy substituents at both ends.<sup>11</sup> By capping more solubilizing polyalkyleneoxy substituents at the ends, highly soluble OPVs containing up to eight phenyl rings have been synthesized. To probe the substitution effect, the asymmetrically end-functionalized OPVs bearing an alkylsulfonyl electron-withdrawing group at one end and polyalkyleneoxy electron-donating group at the other end were also prepared.



OPV(n)-OR

$n = 1-4$ :  $R_1 = \text{OCH}_3$ ,  $R_2 = \text{C}_4\text{H}_9\text{O}(\text{CH}_2\text{CH}_2\text{O})_2$

$n = 5-6$ :  $R_1 = R_2 = \text{C}_4\text{H}_9\text{O}(\text{CH}_2\text{CH}_2\text{O})_2$



OPV(n)-ORSO

$n = 1-3$ :  $R_1 = \text{OCH}_3$ ,  $R_2 = \text{C}_4\text{H}_9\text{O}(\text{CH}_2\text{CH}_2\text{O})_2$ ,  $R_3 = \text{C}_6\text{H}_{13}$  or  $\text{C}_{10}\text{H}_{21}$

$n = 4$ :  $R_1 = R_2 = \text{C}_4\text{H}_9\text{O}(\text{CH}_2\text{CH}_2\text{O})_2$ ,  $R_3 = \text{C}_6\text{H}_{13}$  or  $\text{C}_{10}\text{H}_{21}$

## Experimental Section

<sup>1</sup>H NMR spectra and <sup>13</sup>C NMR spectra were recorded using a Varian INOVA-400 FT NMR spectrometer and are referenced to the residual CHCl<sub>3</sub> 7.24 ppm and to the CDCl<sub>3</sub> 77

ppm, respectively. Electronic absorption (UV–vis) spectra were recorded in chloroform and tetrahydrofuran (THF), respectively, using a Varian Cary 100 Scan spectrophotometer.  $\gamma_{\text{calc}}$  ( $\omega = 0$ ) values were calculated by the PM3 semiempirical calculations using the Finite Field method in Mopac6 in the Alchemy2000 software package as well as by the time-dependent coupled perturbed Hartree–Fock method within the MOPAC93 package. Z-scan measurements were performed in chloroform and THF with a system consisting of a Coherent Mira Ar-pumped titanium-sapphire laser generating a mode-locked train of approximately 100-fs 800-nm pulses and a titanium-sapphire regenerative amplifier pumped by a Q-switched pulsed YAG laser at 30 Hz. The open- and closed-aperture Z-scans were recorded at several concentrations for each compound, and the real and imaginary part of the nonlinear phase shift was determined by numerical fitting. The real and imaginary parts of the hyperpolarizability of the solute were calculated by assuming a linear concentration dependence of the solution susceptibility. The nonlinearities and light intensities were calibrated using measurements of a 1-mm thick silica plate for which the nonlinear refractive index  $n_2 = 3 \times 10^{-16} \text{ cm}^2 \text{ W}^{-1}$  was assumed.

**General Procedure for the Wadsworth–Emmons Reaction.** To a stirred solution of 1:1 equiv of aldehyde (2 equiv of aldehyde for double Wadsworth–Emmons reaction) and the corresponding phosphonate ester in 10–15 mL of anhydrous dimethyl ether (DME) was slowly added about 1.3 equiv of NaH at 0 °C. After stirring for 0.5 h at 0 °C, the reaction mixture was slowly warmed to room temperature. After stirring for 4 h at room temperature, the solution mixture was quenched with water. The crude product was collected by suction filtration. The pure product was isolated by silica gel chromatography using CH<sub>2</sub>Cl<sub>2</sub>/EtOAc as eluent.

**OPV(5)-OR.** The aforesaid procedure was followed using 413 mg (0.52 mmol) aldehyde **1**, 218 mg (0.21 mmol) of bisphosphonate ester **2**, and 26 mg (0.65 mmol) of NaH. The pure product was separated by silica gel column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/EtOAc as eluent, affording 391 g (91%) as a yellow solid. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.51 (s, 12H), 7.49 (s, 8H), 7.12 (s, 8H), 6.97 (s, 4H), 6.76 (s, 4H), 4.23–4.15 (m, 12H), 3.87 (t,  $J = 5.40 \text{ Hz}$ , 8H), 3.80 (t,  $J = 5.13 \text{ Hz}$ , 4H), 3.74–3.69 (m, 12H), 3.61–3.56 (m, 12H), 3.48–3.42 (m, 12H), 1.59–1.51 (m, 12H), 1.41–1.30 (m, 12H), 0.90 (t,  $J = 7.43 \text{ Hz}$ , 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C,  $\delta$ ): 152.8, 138.5, 136.7, 136.6, 132.9, 128.4, 128.1, 127.7, 126.9, 126.8, 106.3, 72.4, 71.2, 70.9, 70.5, 70.1, 69.8, 68.9, 31.7, 19.3, 13.9. MS (FAB)  $m/z$ : 1675.1 ( $M^+ + 23$ ). Anal. Calcd for C<sub>102</sub>H<sub>138</sub>O<sub>18</sub>: C, 74.15; H, 8.41. Found: C, 73.89; H, 8.56; mp: 240–243 °C.

**OPV(6)-OR.** The aforesaid procedure was followed using 172 mg (0.19 mmol) of aldehyde **5**, 218 mg (0.21 mmol) the corresponding phosphonate ester **6**, and 10 mg (0.25 mmol) of NaH. The pure product was separated by silica gel column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/EtOAc as eluent, affording 293 mg (88%) of a yellow solid. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.50 (s, 16H), 7.49 (s, 8H), 7.12 (s, 10H), 6.97 (s, 4H), 6.76 (s, 4H), 4.23–4.15 (m, 12H), 3.87 (t,  $J = 5.13 \text{ Hz}$ , 8H), 3.80 (t,  $J = 5.13 \text{ Hz}$ , 4H), 3.74–3.69 (m, 12H), 3.61–3.56 (m, 12H), 3.48–3.42 (m, 12H), 1.66–1.51 (m, 12H), 1.40–1.24 (m, 12H), 0.90 (t,  $J = 7.29 \text{ Hz}$ , 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C,  $\delta$ ): 152.8, 138.5, 136.6, 132.9, 130.6, 128.8, 128.4, 128.1, 127.7, 126.9, 106.3, 72.4, 71.2, 70.8, 70.5, 70.1, 69.8, 68.9, 31.7, 19.3, 13.9. MS (FAB)  $m/z$ : 1777.3 ( $M^+ + 23$ ). Anal. Calcd for C<sub>110</sub>H<sub>144</sub>O<sub>18</sub>: C, 75.31; H, 8.27. Found: C, 75.57; H, 8.39; mp: 220–225 °C.

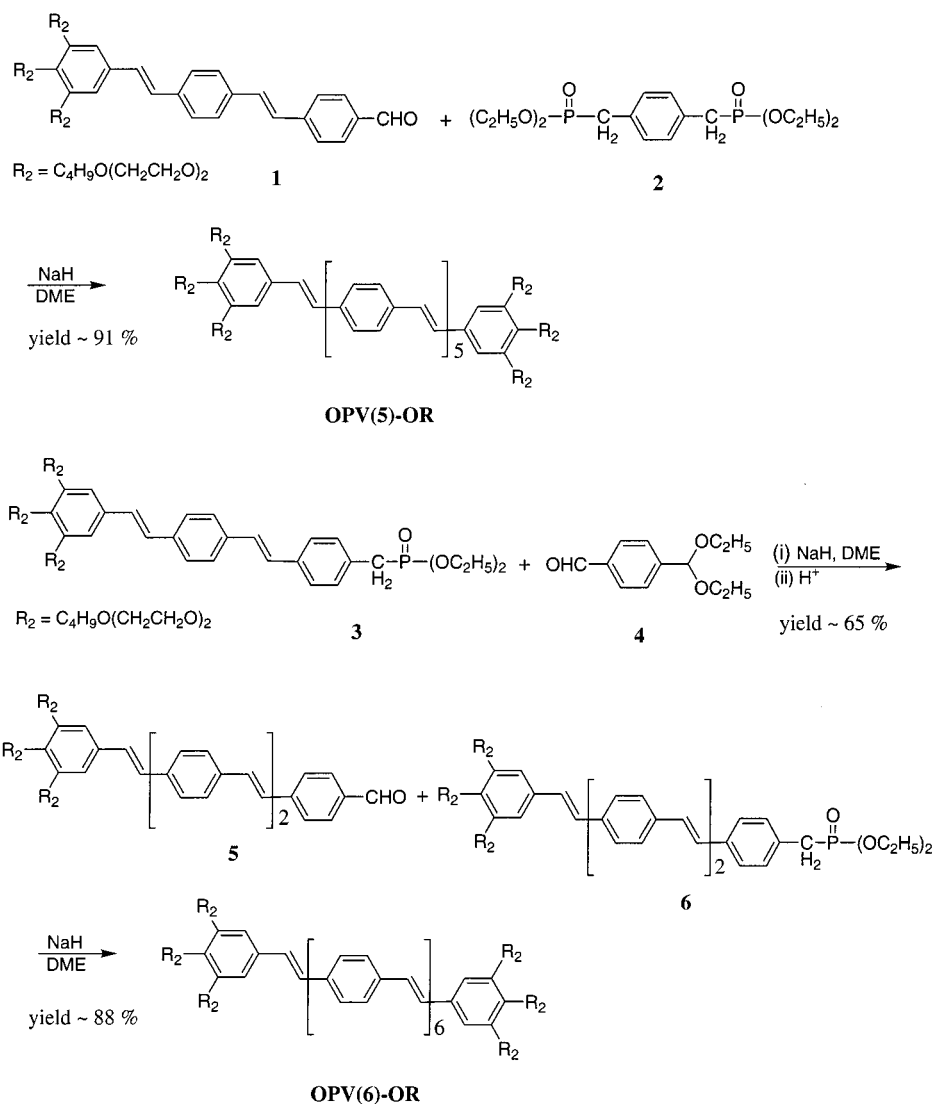
**OPV(1)-ORSO ( $R_3 = \text{C}_{10}\text{H}_{21}$ ).** The aforesaid procedure was followed using 95 mg (0.29 mmol) of aldehyde **11**, 140 mg (0.29 mmol) of phosphonate ester **9**, and 15 mg (0.38 mmol) of NaH. The pure product was separated by silica gel column chromatography using 16:1 of CH<sub>2</sub>Cl<sub>2</sub>/EtOAc as eluent, affording 147 mg (78%) of a yellow solid. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.85 (d,  $J = 8.10 \text{ Hz}$ , 2H), 7.65 (d,  $J = 8.37 \text{ Hz}$ , 2H), 7.51 (s, 4H), 7.23 (d,  $J = 16.47 \text{ Hz}$ , 1H), 7.12 (d,  $J = 16.47 \text{ Hz}$ , 1H), 7.06 (d,  $J = 16.2 \text{ Hz}$ , 1H), 6.98 (d,  $J = 16.2 \text{ Hz}$ , 1H), 6.72 (s, 2H), 4.16 (t,  $J = 5.13 \text{ Hz}$ , 2H), 3.88 (s, 6H), 3.81 (t,  $J = 5.13 \text{ Hz}$ , 2H), 3.71–3.69 (m, 2H), 3.61–3.57 (m, 2H), 3.45 (t,  $J = 6.62 \text{ Hz}$ ,

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## Scheme 1. Syntheses of OPv(5)-OR and OPv(6)-OR

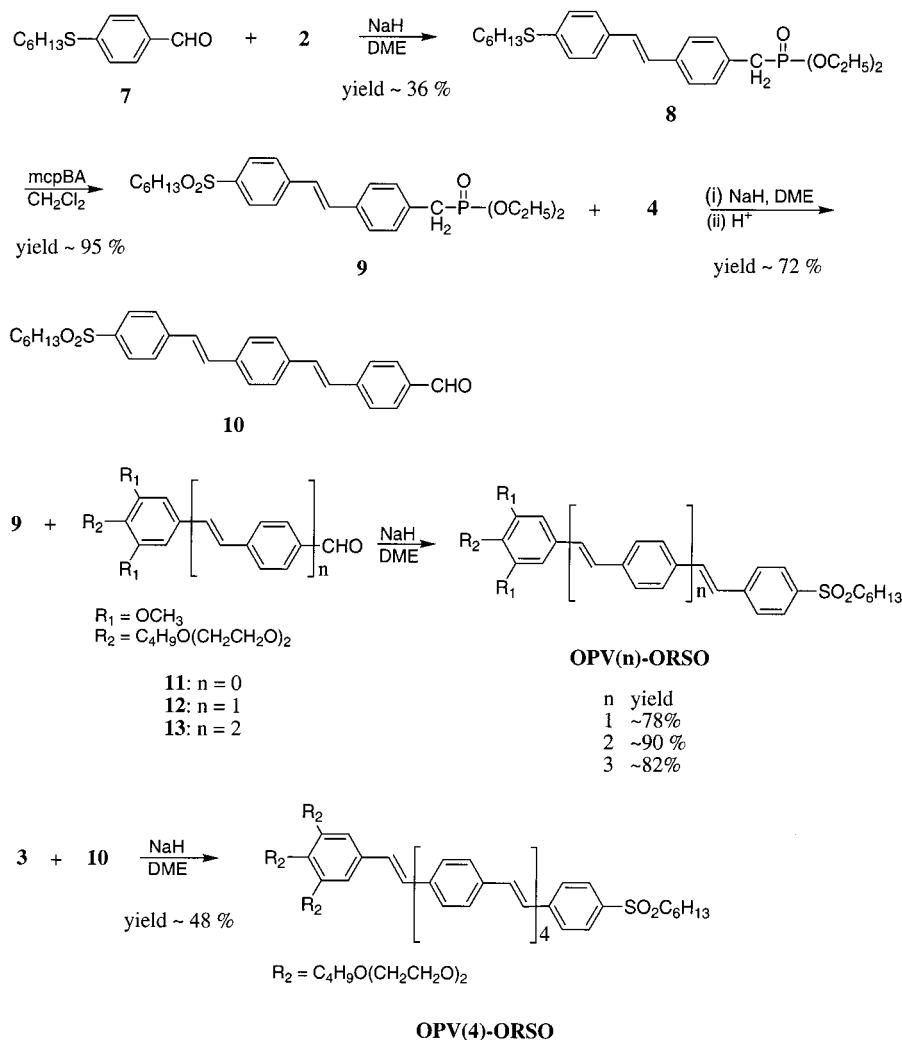


2H), 3.07 (t,  $J = 8.10$  Hz, 2H), 1.70–1.39 (m, 4H), 1.21 (m, 16H), 0.92–0.81 (m, 6H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ , 25 °C,  $\delta$ ): 153.5, 142.7, 137.6, 137.3, 137.2, 135.5, 132.8, 132.0, 129.2, 128.5, 127.4, 127.3, 126.9, 126.8, 126.3, 103.7, 72.3, 71.2, 70.6, 70.3, 70.1, 56.4, 56.1, 31.8, 31.6, 29.6, 29.3, 29.2, 28.9, 28.2, 22.7, 22.6, 19.2, 14.0, 13.9. MS (FAB)  $m/z$ : 706.9 ( $M^+$ ). HRMS (FAB): calcd for  $C_{42}H_{58}O_7NaS$ , 729.3801; found, 729.3814; mp: 170 °C.

**OPV(2)-ORSO ( $R_3 = C_{10}H_{21}$ ).** The aforesaid procedure was followed using 214 mg (0.5 mmol) of aldehyde **12**, 287 mg (0.6 mmol) of phosphonate ester **9**, and 26 mg (0.65 mmol) of NaH. The pure product was separated by silica gel column chromatography using 16:1 of  $CH_2Cl_2$ /EtOAc as eluent, affording 339 mg (90%) of a yellow solid.  $^1H$  NMR (270 MHz,  $CDCl_3$ ,  $\delta$ ): 7.86 (d,  $J = 8.10$  Hz, 2H), 7.66 (d,  $J = 8.64$  Hz, 2H), 7.53 (s, 4H), 7.50 (s, 4H), 7.31 (d,  $J = 16.47$  Hz, 1H), 7.12 (d,  $J = 15.93$  Hz, 1H), 7.13 (s, 2H), 7.06 (d,  $J = 16.47$  Hz, 1H), 6.98 (d,  $J = 16.47$  Hz, 1H), 6.72 (s, 2H), 4.16 (t,  $J = 5.13$  Hz, 2H), 3.89 (s, 6H), 3.81 (t,  $J = 5.13$  Hz, 2H), 3.72–3.69 (m, 2H), 3.61–3.57 (m, 2H), 3.45 (t,  $J = 6.62$  Hz, 2H), 3.08 (t,  $J = 8.24$  Hz, 2H), 1.70–1.39 (m, 4H), 1.21 (m, 16H), 0.92–0.81 (m, 6H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ , 25 °C,  $\delta$ ): 153.5, 142.7, 137.7, 137.4, 137.1, 136.8, 136.4, 135.6, 133.0, 132.1, 128.8, 128.7, 128.5, 127.8, 127.6, 127.3, 126.9, 126.8, 126.4, 103.7, 72.3, 71.2, 70.6, 70.4, 70.1, 56.4, 56.1, 31.8, 31.7, 29.6, 29.4, 29.2, 28.9, 28.2, 22.7, 22.6, 19.2, 14.0, 13.9. MS (FAB)  $m/z$ : 809.6 ( $M^+$ ). HRMS (FAB): calcd for  $C_{50}H_{64}O_7NaS$ , 831.4270; found, 831.4261; mp: 200 °C.

**OPV(3)-ORSO ( $R_3 = C_6H_{13}$ ).** The aforesaid procedure was followed using 175 mg (0.33 mmol) of aldehyde **13**, 158 mg (0.33 mmol) of phosphonate ester, and 17 mg (0.43 mmol) of NaH. The pure product was separated by silica gel column chromatography using 16:1 of  $CH_2Cl_2$ /EtOAc as eluent, affording 236 mg (82%) of a yellow solid.  $^1H$  NMR (270 MHz,  $CDCl_3$ ,  $\delta$ ): 7.86 (d,  $J = 8.10$  Hz, 2H), 7.66 (d,  $J = 8.37$  Hz, 2H), 7.53 (s, 4H), 7.51 (s, 4H), 7.50 (s, 4H), 7.12 (bm, 6H), 7.03 (m, 2H), 6.72 (s, 2H), 4.16 (t,  $J = 5.13$  Hz, 2H), 3.89 (s, 6H), 3.81 (t,  $J = 5.13$  Hz, 2H), 3.72–3.69 (m, 2H), 3.61–3.57 (m, 2H), 3.46 (t,  $J = 6.62$  Hz, 2H), 3.08 (t,  $J = 8.24$  Hz, 2H), 1.70–1.39 (m, 4H), 1.21 (m, 8H), 0.92–0.81 (m, 6H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ , 25 °C,  $\delta$ ): 153.5, 142.7, 137.7, 137.4, 137.1, 136.8, 136.4, 135.6, 133.0, 132.1, 128.8, 128.7, 128.6, 127.8, 127.6, 127.3, 126.9, 127.3, 126.9, 103.7, 72.3, 71.2, 70.6, 70.4, 70.1, 56.4, 56.2, 31.7, 31.1, 29.7, 28.0, 22.7, 22.3, 19.2, 13.9. MS (FAB)  $m/z$ : 854.8 ( $M^+ + 23$ ). Anal. Calcd for  $C_{52}H_{62}O_7S$ : C, 75.15; H, 7.52; S, 3.86. Found: C, 75.03; H, 7.40; S, 3.71; mp: 256–258 °C.

**OPV(4)-ORSO ( $R_3 = C_6H_{13}$ ).** The aforesaid procedure was followed using 69 mg (0.15 mmol) of aldehyde **10**, 137 mg (0.15 mmol) of phosphonate ester **3**, and 15 mg (0.38 mmol) of NaH. The pure product was separated by silica gel column chromatography using 16:1 of  $CH_2Cl_2$ /EtOAc as eluent, affording 88 mg (48%) of a yellow solid.  $^1H$  NMR (270 MHz,  $CDCl_3$ ,  $\delta$ ): 7.86 (d,  $J = 8.10$  Hz, 2H), 7.66 (d,  $J = 8.37$  Hz, 2H), 7.53–7.48 (m, 16H), 7.16–7.12 (m, 8H), 6.94 (m, 2H), 6.76 (s, 2H), 4.22–4.15 (m, 6H), 3.87 (t,  $J = 4.00$  Hz, 4H), 3.80 (t,  $J = 5.27$  Hz, 2H),

Scheme 2. Syntheses of OPV(*n*)-ORSO, *n* = 1–4

3.74–3.69 (m, 6H), 3.61–3.58 (m, 6H), 3.48–3.42 (m, 6H), 3.08 (t, *J* = 7.83 Hz, 2H), 1.74–1.51 (m, 8H), 1.41–1.24 (m, 12H), 0.92–0.82 (m, 12H). MS (FAB) *m/z*: 1240.1 (*M*<sup>+</sup> + 23). Anal. Calcd for C<sub>76</sub>H<sub>96</sub>O<sub>11</sub>S: C, 74.86; H, 7.94. Found: C, 74.61; H, 8.05; mp: 215 °C (dec).

## Results and Discussion

Several strategies have been developed to synthesize homologue series of laterally substituted OPVs in the past few years.<sup>12–16</sup> We have used the stereoselective Wadsworth–Emmons reaction as a key step to construct the all-trans carbon–carbon double bonds of the end-functionalized OPVs. The higher homologue of symmetrically substituted OPVs, OPV(*n*)-OR, *n* = 5–6, and asymmetrically substituted OPVs, OPV(*n*)-ORSO, *n* = 1–4, were first synthesized using the strategy established previously.<sup>11</sup> The general synthetic sequences for the newly developed OPVs are summarized in Schemes 1 and 2. The seven-phenyl-ring oligomer, OPV(5)-OR,

was synthesized by the double Wadsworth–Emmons reactions of tripolyalkyleneoxy-substituted styrylstyrylbenzaldehyde, **1**, and bis(diethyl)-*p*-xylylene-bis(phosphonate), **2**. The eight-phenyl-ring oligomer, OPV(6)-OR, was prepared by a 4 + 4 convergent approach in which four-phenyl-ring aldehyde **5** was reacted with the four-phenyl-ring phosphonate **6** in the presence of NaH in DME. In a similar fashion, the asymmetrically substituted OPVs were synthesized by the Wadsworth–Emmons reactions of 4-(alkylsulfonyl)-4'-styrylbenzylphosphonate, **9**, and the corresponding aldehyde (**11**, **12**, or **13**), affording the desired OPV(*n*)-ORSO (*n* = 1, 2, and 3, respectively) in good yields as shown in Scheme 2. To enhance the solubility of OPV(4)-ORSO, tripolyalkyleneoxy end groups were again needed. OPV(4)-ORSO was prepared by the Wadsworth–Emmons reactions of three-phenyl-ring phosphonate **3** and three-phenyl-ring aldehyde **10**. All of the new synthesized OPVs were soluble in common organic solvents and fully characterized by standard spectroscopic techniques including <sup>1</sup>H NMR, <sup>13</sup>C NMR, and low/high-resolution mass spectroscopy (FAB) or elemental analysis.

The Z-scan technique,<sup>17</sup> which can determine the sign, the real part of the molecular nonlinearity γ<sub>real</sub> (which

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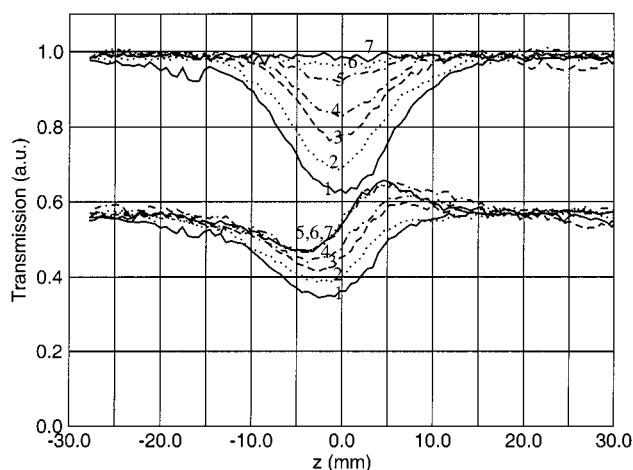


**Table 1. Results of the Physical Measurements and PM3 Semiempirical Calculations of OPV(*n*)-OR<sup>a</sup>, *n* = 1–6**

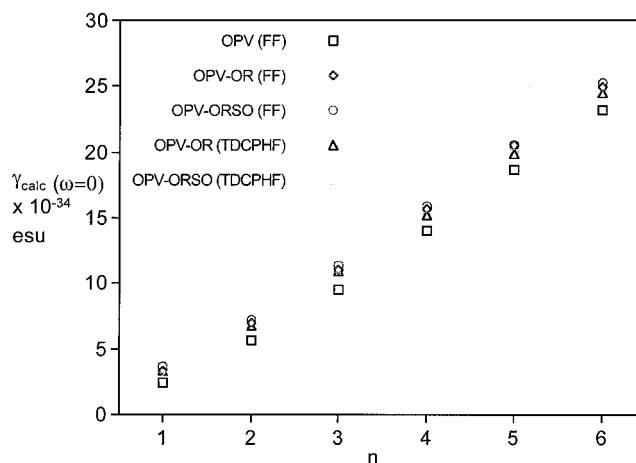
<i>n</i>	$\lambda_{\max}$ (nm) [ $\epsilon_{\max}$ ( $\times 10^{-4}$ $\text{M}^{-1} \text{cm}^{-1}$ )] in $\text{CHCl}_3$	$\gamma_{\text{real}}$ in $\text{CHCl}_3$ ( $\times 10^{-36}$ esu)	$\gamma_{\text{imag}}$ in $\text{CHCl}_3$ ( $\times 10^{-36}$ esu)	$ \gamma $ in $\text{CHCl}_3$ ( $\times 10^{-36}$ esu)	$\lambda_{\max}$ in THF (nm)	$\gamma_{\text{real}}$ in THF ( $\times 10^{-36}$ esu)	$\gamma_{\text{imag}}$ in THF ( $\times 10^{-36}$ esu)	$ \gamma $ in THF ( $\times 10^{-36}$ esu)	$\gamma_{\text{calc}}(\omega = 0)^b$ ( $\times 10^{-36}$ esu) (FF) <sup>c</sup>	$\gamma_{\text{calc}}(\omega = 0)^b$ ( $\times 10^{-36}$ esu) (TDCPHF) <sup>d</sup>
1	371 (6.2)	140 ± 50	80 ± 30	160 ± 60	371	390 ± 80	130 ± 30	410 ± 90	336	331
2	392 (9.2)	−130 ± 50	350 ± 50	370 ± 60	393	70 ± 150	400 ± 100	410 ± 120	695	679
3	406 (10.7)	−740 ± 250	1120 ± 300	1350 ± 390	407	−430 ± 200	2000 ± 300	2050 ± 340	1105	1094
4	413 (11.7)	−2800 ± 1500	1170 ± 500	3040 ± 1580	414	−4000 ± 2000	3600 ± 2000	5380 ± 2830	1566	1526
5	418 (15.1)	−21100 ± 5000	13990 ± 3000	25320 ± 5830	418	−5500 ± 3000	10200 ± 5000	11590 ± 5830	2048	1990
6	421 (14.3)	−11480 ± 5000	7230 ± 3000	13560 ± 5830					2491	2451

<sup>a</sup> For simplicity, R=CH<sub>3</sub> is used in the calculations. <sup>b</sup> Calculated molecular nonlinearity  $\gamma$  at zero frequency. <sup>c</sup> Finite Field method.<sup>d</sup> Time-dependent coupled perturbed Hartree–Fock method and converted from atomic units using the relation of 1 atomic unit = 5.036 86  $\times 10^{-40}$  esu.**Table 2. Results of the Physical Measurements and PM3 Semiempirical Calculations of OPV(*n*)-ORSO<sup>a</sup>, *n* = 1–4**

<i>n</i>	$\lambda_{\max}$ (nm) [ $\epsilon_{\max}$ ( $\times 10^{-4}$ $\text{M}^{-1} \text{cm}^{-1}$ )] in $\text{CHCl}_3$	$\gamma_{\text{real}}$ in $\text{CHCl}_3$ ( $\times 10^{-36}$ esu)	$\gamma_{\text{imag}}$ in $\text{CHCl}_3$ ( $\times 10^{-36}$ esu)	$ \gamma $ in $\text{CHCl}_3$ ( $\times 10^{-36}$ esu)	$\lambda_{\max}$ in THF (nm)	$\gamma_{\text{real}}$ in THF ( $\times 10^{-36}$ esu)	$\gamma_{\text{imag}}$ in THF ( $\times 10^{-36}$ esu)	$ \gamma $ in THF ( $\times 10^{-36}$ esu)	$\gamma_{\text{calc}}(\omega = 0)^b$ ( $\times 10^{-36}$ esu) (FF) <sup>c</sup>	$\gamma_{\text{calc}}(\omega = 0)^b$ ( $\times 10^{-36}$ esu) (TDCPHF) <sup>d</sup>
1	373 (5.8)	−3 ± 100	550 ± 60	550 ± 60	373	260 ± 50	450 ± 80	520 ± 90	364	363
2	393 (8.3)	−1240 ± 200	760 ± 150	1460 ± 250	394	−310 ± 150	980 ± 100	1030 ± 140	720	711
3	406 (10.9)	−5240 ± 1500	1950 ± 500	5590 ± 1580	405	−5530 ± 2000	3230 ± 1500	6410 ± 2480	1140	1121
4	415 (8.7)	−3970 ± 1500	3190 ± 800	5090 ± 1670	413	−5000 ± 5000	4910 ± 2000	7010 ± 4970	1580	1564

<sup>a</sup> For simplicity, R=CH<sub>3</sub> is used in the calculations. <sup>b</sup> Calculated molecular nonlinearity  $\gamma$  at zero frequency. <sup>c</sup> Finite Field method.<sup>d</sup> Time-dependent coupled perturbed Hartree–Fock method and converted from atomic units using the relation of 1 atomic unit = 5.036 86  $\times 10^{-40}$  esu.**Figure 1.** Open (upper set of curves) and closed (lower set of curves) aperture Z-scans performed on THF solutions of OPV(6)-OR. The concentrations are (1) 2.88%, (2) 1.95%, (3) 1.01%, (4) 0.602%, (5) 0.242%, (6) 0.100%, and (7) 0.034%. All scans were performed with 100-fs pulses at 800 nm, the Gaussian beam parameter  $w_0 = 38 \mu\text{m}$ , and the light intensity was about 60 GW/cm<sup>2</sup>.

relates to the refractive nonlinearity), and the imaginary part of the molecular nonlinearity  $\gamma_{\text{imag}}$  (due to the multiphoton absorption), was used to determine the third-order optical nonlinearities of these end-functionalized OPVs. The Z-scan measurements were performed at 800 nm with 100-fs laser pulses in two different solvents, chloroform and THF. Figure 1 shows the experimental Z-scan curves measured with different concentrations of OPV(6)-OR. The molecular nonlinearities,  $\gamma_{\text{calc}}$  (at zero frequency), were calculated by the PM3 semiempirical calculations using the Finite Field method in MOPAC6 and by the time-dependent coupled perturbed Hartree–Fock method within the MOPAC93 package. Results of physical measurements and PM3 semiempirical calculations for OPV(*n*)-OR and OPV(*n*)-ORSO are tabulated in Tables 1 and 2, respectively.

**Figure 2.** Plots of  $\gamma_{\text{calc}}(\omega = 0)$  calculated by the Finite Field method (FF) and the time-dependent coupled perturbed Hartree–Fock method (TDCPHF) of OPV, OPV(*n*)-OR, and OPV(*n*)-ORSO versus the phenylenevinylene unit, *n*.

Both variations of the MOPAC package predict a similar pattern of the increase of  $\gamma_{\text{calc}}(\omega = 0)$  with the length of the molecule. The increase with the number of conjugated units is slightly superlinear. On the other hand, the semiempirically predicted differences between the symmetric and asymmetric molecules are relatively small. Also, the  $\gamma$  enhancement contributed by the substituents becomes comparatively less significant as the chain length increases, indicating an importance of the extended delocalization to enhance  $\gamma$  (Figure 2). The experimentally obtained values are, clearly, presenting the case for the importance of the frequency dispersion of the molecular hyperpolarizabilities. Comparison of the values of  $|\gamma|$  is perhaps of more immediate value than looking at the separated values of the real and imaginary parts of the hyperpolarizabilities. In both the OPV(*n*)-OR and OPV(*n*)-ORSO series, there is a sequential increase in  $|\gamma|$  as the conjugation length (*n*) increases. However, the pattern of the increase is more

complicated than the predictions calculated from in MOPAC package. In the OPV(*n*)-OR series,  $|\gamma|$  appears to approach saturation (maximum) at  $n = 5$ . This may be, however, misleading because of both the issue of experimental inaccuracies and, in particular, the influence of dispersion which modifies the  $\gamma$  values as the resonance of the doubled frequency of the used laser (i.e., the wavelength of 400 nm) traverses the range of frequencies of the excited levels of the molecules. A particularly telltale indication of the importance of this near-resonance behavior is the change in the sign of  $\gamma_{\text{real}}$  from positive to negative with an increase in the length of the molecules. It is surprising that the sign reversal from positive to negative occurs earlier in chloroform than in THF, even though the absorption behavior of all molecules in both solvents is very similar. Fine details of the energetic structure of molecules in solution must play a role here. In a similar way, although OPV(*n*)-ORSO and OPV(*n*)-OR show very similar absorption behavior,  $|\gamma|$  of OPV(*n*)-ORSO appears to be larger than that of the corresponding OPV(*n*)-OR for low *n* values, confirming an advantage of using donor–acceptor asymmetric substitution to enhance molecular nonlinearities,<sup>18</sup> in particular alkylsulfonyl-polyalkyleneoxy pair.<sup>19</sup> However, the higher homologues of the oligomers do not benefit to a greater extent from such cascading effect. In fact, it appears that the OPV(*n*)-ORSO series exhibits a faster convergence of  $|\gamma|$  than the symmetrically substituted OPV(*n*)-OR series. As a result, the higher homologue of symmetrically substituted OPVs-OPV(5)-OR exhibit the largest  $|\gamma|$  ( $2.5 \times 10^{-32}$  esu) among the oligomeric systems reported, indicating the importance of the coplanarity and long conjugated length. It is difficult and inappropriate to compare the measured  $|\gamma|$  of the related systems among various laboratories, as the experimental conditions and techniques used in each laboratory vary significantly. Nevertheless, OPV(5)-OR exhibits a  $|\gamma|$  value that is among the highest obtained by us so far for organic and organometallic molecules with femtosecond laser pulses at 800 nm.<sup>20–22</sup>

In a series of symmetric polyenovanillines possessing a sequence of conjugated double bonds capped with

solubilizing groups substituted phenyl moieties, the sign of  $\gamma_{\text{real}}$  is positive in the lower homologue of oligomers and changes sign to negative for longer oligomers.<sup>23</sup> In addition, the linear spectroscopic properties and third-order optical nonlinearities of studied polyenes varied in various solvent environments. Thus, the two cases, that of the polyenovanillines reported previously and that of oligophenylenevinyls presented in this paper, may provide the first published indications that solvent effects are quite important for third-order nonlinearities of  $\pi$ -conjugated molecules investigated in solutions. At present, it is unclear whether the effects can be fully understood in terms of the solvent-induced changes of the energetic structure of the molecules (and, in particular, those parameters of the excited states which are the most relevant for the third-order nonlinearity, such as the position of the two-photon resonant level). Further investigations are necessary to clarify these issues. It is, however, gratifying that the theoretical predictions made using simple semiempirical techniques are, at least, not in drastic disagreement with the experimental results. An important step toward reconciling the experimental data with the theoretical ones would be the calculation of frequency-dependent (including damping) hyperpolarizabilities for the oligomers. Understanding of solvent effects should then become an issue of deciding whether the solvent-induced frequency shifts of the most relevant levels explain the observed behavior.

In summary, we have synthesized novel series of symmetrically and asymmetrically end-functionalized coplanar OPVs containing up to eight phenyl rings and investigated, theoretically and experimentally, their third-order NLO properties. In contrast to the Z-scan determined  $\gamma$ , the calculated  $\gamma$  show a monotonic increase with an extension of chain length in both series. However, the Z-scan determined  $\gamma$  values are found to be solvent-dependent, even though the solvent polarities are similar. The  $\gamma$  enhancement contributed by the cascading effect in the asymmetrically disubstituted OPVs appears less significant when the chain length increases. In addition, the asymmetrically disubstituted OPVs show a faster convergence of  $|\gamma|$  than the symmetrically disubstituted series. A very large  $|\gamma|$  value, up to  $2.5 \times 10^{-32}$  esu, was obtained in the symmetrically disubstituted OPVs, suggesting the importance of the coplanarity and long conjugated length.

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