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Two-Photon Properties and Excitation Dynamics of Poly(*p*-phenylenevinylene) Derivatives Carrying Phenylanthracene and Branched Alkoxy Pendents†

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This paper presents a study of excitation dynamics and two-photon properties in new branched poly(*p*-phenylenevinylene) structures which can be viewed as composed of interlinked structural units producing localized but interacting electronic excitations. Poly(*p*-phenylenevinylene) (PPV) derivatives, specifically poly-[2-(9-phenylanthracen-10-yl)-1,4-phenylenevinylene] (**P-1**) and poly[2-(2-ethylhexyloxy)-5-(9-phenylanthracen-10-yl)-1,4-phenylenevinylene] (**P-2**), carrying 9-phenylanthracene pendent were prepared, and their one- and two-photon absorption and emission properties were studied in solution. **P-1** and **P-2** differ in structure by the presence of additional 2-ethylhexyloxy pendent groups in **P-2**. Both polymers were prepared by direct polymerization of the α,α′-dibromo-*p*-xylene monomers having the pendent group(s) in the present of excess potassium *tert*-butoxide. For the sake of comparison, 9,10-diphenylanthracene (DPA) and poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] [Meh-PPV (**P-3**)] were also included in our study. From nanosecond and femtosecond nonlinear transmission measurements, their effective two-photon cross sections (σ_{TPA}) at ∼ 800 nm were found to be 11.9 × 10^{-20} for **P-1**, 66.6 × 10^{-20} for **P-2**, and 44.0 × 10^{-20} for **P-3** in nanosecond pulses and 0.074 × 10^{-20} for **P-1**, 0.196 × 10^{-20} for **P-2**, and 0.168 × 10^{-20} cm^4/GW for **P-3** in femtosecond pulses, respectively. Their two-photon excitation spectra were also studied. **P-2** having both the phenylanthrace and alkoxy pendents exhibits the best performance as a two-photon absorber in both of nano- and femtosecond measurements at ∼800 nm. Furthermore, a complete energy transfer from the pendent phenylanthracene moiety to the PPV backbone is observed.

Introduction

A wide variety of conjugated polymers have been reported in the past decades as electroactive materials for diverse applications such as batteries, molecular electronic devices, nonlinear optical switches, and light-emitting diodes (LEDs), etc.[1−5] Among them, PPV and its derivatives have received considerable attention because of their feasibilities in tuning electrical and optical properties.[6−8] Processable PPV derivatives and PPV itself have been used to form an active layer in thin-film light emitting diodes (LEDs) with promising efficiencies.[9−11] By tuning the morphologies, band gaps, and charge-transport properties of these polymers, device stabilities have been increased, and emitters at a wide variety of wavelengths have been fabricated.[12−14] Recently, superradiance in the PPV and its derivatives have been achieved,[15] suggesting the prospect of polymer semiconductor lasers. PPV formed in pores of a glass have shown tunable lasing. PPV also exhibits a strong two-photon pumped up-conversion emission when excited by near-IR laser pulses of 800 nm.[16,17] This opens another prospect, that of up-conversion lasing.

Two-photon absorption (TPA) is a nonlinear optical process in which two photons of longer wavelength are simultaneously absorbed by a chromophore that would normally be excited by a single photon with a shorter wavelength. As a result, whereas the rate of single-photon absorption scales linearly with the intensity of incident radiation, the rate of TPA scales quadratically. Since pioneering work by Rentzepis in optical data storage[18,19] and by Webb in optical microscopy[20,21] that demonstrated early potential application of two-photon processes, there has been considerable interest in the design, synthesis and characterization of new organic chromophores and polymers with potentially large two-photon absorption cross sections. Potential photonic applications for two-photon chromophores and polymers include two-photon upconversion lasing,[22,23] two-photon power limiting,[24,25] three-dimensional optical data storage,[26,27] two-photon microfabrication,[28,29] and two-photon photodynamic cancer therapy.[30,31]

Recently, our work has focused on the designs and studies of branched conjugated structures which can produce one and two-photon excitations localized in various segments of their molecular structures.[32] These types of structures provide two-photon absorption over a broad spectral range and also produce efficient excitation transfer from one segment to another.

We reported earlier photoluminescence (PL) and electroluminescence (EL) characteristics in the thin films of PPV with its derivatives carrying 9-phenylanthracene pendent, poly[2-(9-

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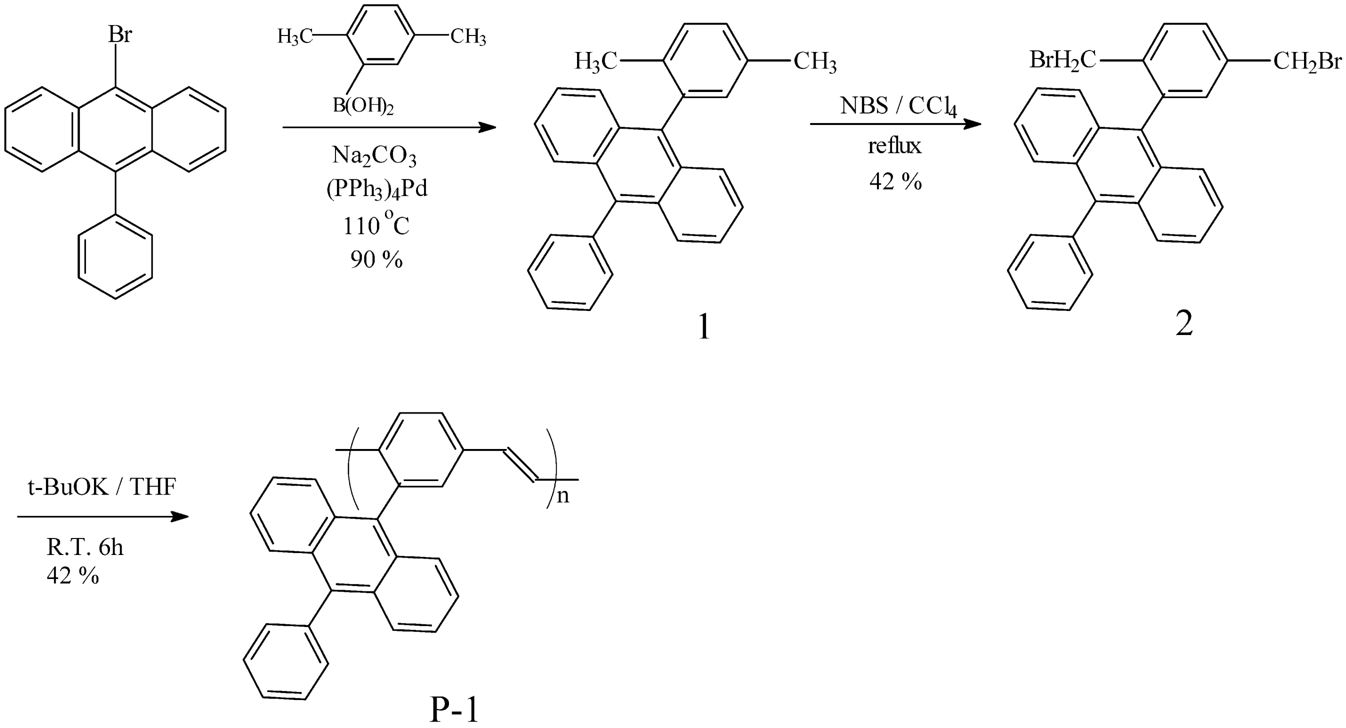
SCHEME 1: Synthetic Route to P-1



phenylanthracen-10-yl)-1,4-phenylenevinylene] (**P-1**), and both the phenylanthracene and 2-ethylhexyloxy substituent, poly[2-(2-ethylhexyloxy)-5-(9-phenylanthracen-10-yl)-1,4-phenylenevinylene] (**P-2**). These polymers can be viewed as composed of the interlinked structures. These two PPV derivatives are soluble in organic solvents and **P-2** revealed a greatly enhanced power efficiency in EL devices when compared with PPV and **P-1**.[33,34]

In this article, we report the synthesis, structural characterizations and optical properties including two-photon absorption (TPA) of these two PPV derivatives containing phenylanthracene moiety and also the 2-ethylhexyloxy substituent as an electron donating group. For the sake of comparison, Meh-PPV (**P-3**)[9,12] and diphenylanthracene (DPA) are also included in the present work. Their TPA properties were investigated by the nonlinear transmission method utilizing nanosecond transmission and the femtosecond Z-scan techniques to obtain the effective two-photon absorption cross section and to examine the effect of pulse-width on the effective cross section.

Results and Discussion

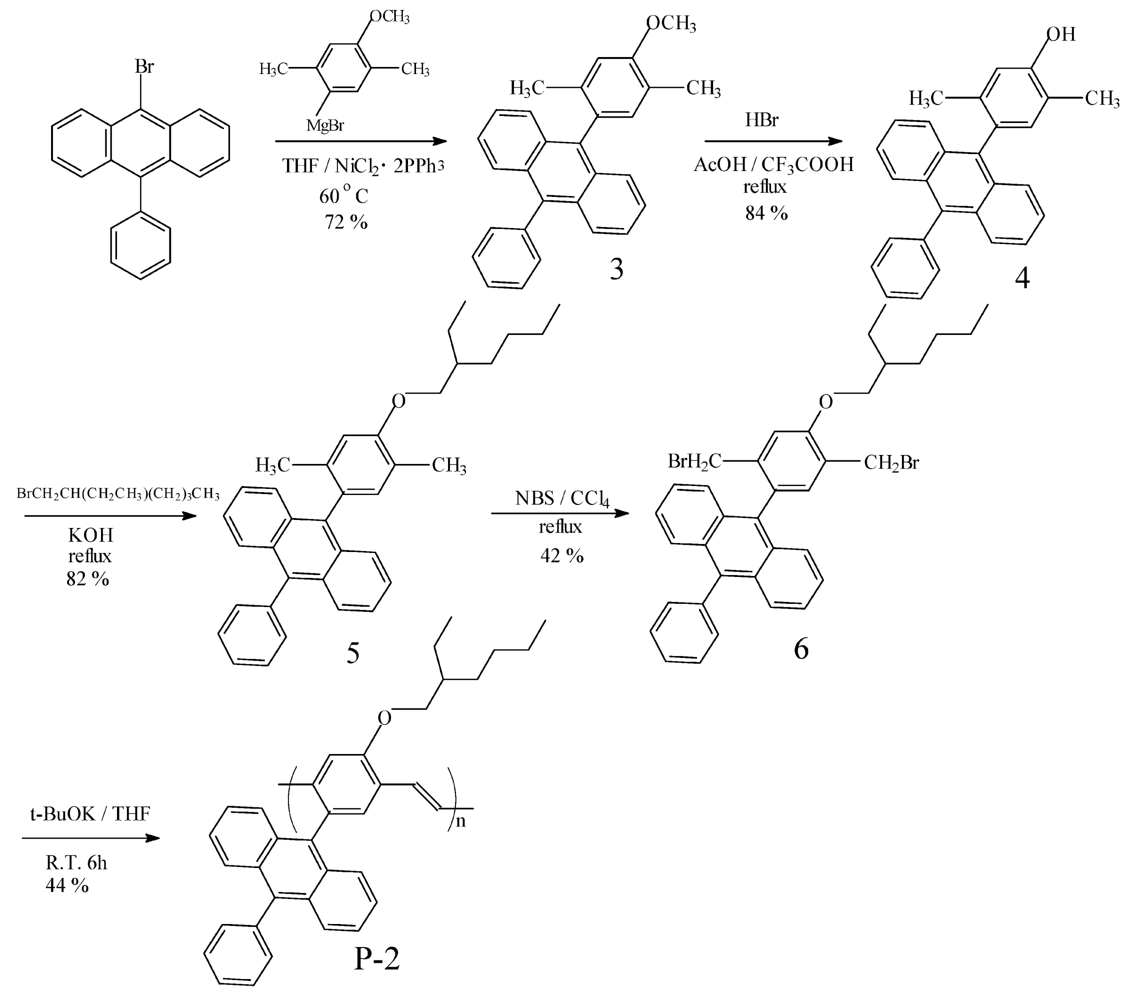
Syntheses of Monomers 2 and 6. P-1 and **P-2** were synthesized by polymerizing bis(bromophenyl)monomers, 2-(9-phenylanthracen-10-yl)-1,4-bis(bromomethyl)benzene (**2**) and 2-ethylhexyloxy-5-(9-phenylanthracen-10-yl)-1,4-bis(bromomethyl)benzene (**6**), which were prepared via the multistep route shown in Schemes 1 and 2, respectively. For the synthesis of monomer **2**, we had to synthesize 2-(9-phenylanthracen-10-yl)-*p*-xylene (**1**) by the Suzuki reaction[35] with 9-bromo-10-phenylanthracene and 2,5-dimethylphenyl boronic acid in the presence of the tetrakis(triphenylphosphine) palladium (0) catalyst. Finally, compound **1** was treated with *N*-bromosuccinimide (NBS) using benzoyl peroxide (BPO) as the initiator, to produce the benzylic bromides in 42% yield. The second monomer, 2-ethylhexyloxy-5-(9-phenylanthracen-10-yl)-1,4-bis(bromomethyl) benzene (**6**), was synthesized in a similar fashion, but its synthesis is a little bit more complicated because the monomer bears the 2-ethylhexyloxy group on the phenyl ring. Compound **3** was prepared from 9-bromo-10-phenylanthracene and 2,5-dimethyl-methoxyphenylmagnesium bromide in the presence of $NiCl_2 \cdot 2PPh_3$ as catalysts.[36] The methoxy group in the compound **3** was deprotected to the corresponding phenolic compound **4** by acidic cleavage of the ether linkage, which then was reacted in ethanol with 2-ethylhexylbromide in the presence of KOH to produce compound **5**. Finally, monomer **6** was synthesized via benzylic bromination of compound **5** using *N*-bromosuccinimide (NBS) and benzoyl peroxide (BPO) as utilized in the synthesis of monomer **6**. The structures of all of the intermediates and the final monomers were confirmed by FT-IR and ^1H NMR spectroscopy and also by elemental analysis.

Syntheses and Properties of Polymers P-1 and P-2. Both polymers were prepared by polymerization of respective monomers at room temperature in THF in the presence of a strong base, potassium *tert*-butoxide. This synthetic method was originally described by Gilch and Wheelwright.[37] This method requires the use of excess alkali to ensure the formation of the fully eliminated structure as shown in Schemes 1 and 2. The mechanism of the polymerization process is two steps: formation of the benzylic anion which links the monomers via an *SN 2* reaction, followed by dehydrohalogenation. Both polymers were purified by reprecipitation using methanol. Their structures were confirmed by FT-IR, ^1H NMR, and elemental analysis.

The polymers are soluble in organic solvents such as toluene, xylene, chloroform, and 1,1,2,2-tetrachloroethane. Their average molar mass measured by gel permeation chromatography (GPC) was $Mn = 44000$ for **P-1** and 34000 for **P-2**, respectively. Toluene was employed as an eluent and polystyrene as standard. The polydispersity index for **P-1** and **2** were 2.42 and 2.27, respectively.

The glass transition temperatures (Tg) of polymer samples cannot be detected up to 300 °C by differential scanning calorimetry (DSC). In TGA analyses, both polymers did not lose any weight up to 300 °C and started to under go fast weight

SCHEME 2: Synthetic Route to P-2



loss from about 370 °C for **P-1** and 350 °C for **P-2**, respectively. The weight loss at high temperature is ascribed to thermal degradation. The presence of the alkoxy substituent appears to reduce the thermal stability of **P-2** when compared with that of **P-1**.

Linear Optical Properties of Polymer Solutions. Figure 2a compares the UV−vis absorption spectra of the PPV derivatives along with that of DPA, obtained in 1,1,2,2-tetrachloroethane solutions. The spectra can be analyzed by considering the polymers as composed of two types of interlinked structure: a diphenylanthracene moiety and a derivatized PPV type main backbone. The polymers carrying phenylanthracene commonly exhibit strong four vibronic absorption bands at about 325−410 nm overlapped with a weaker and broader absorptions at a longer wavelength region that arise from the electronic−transition of the main chain−system. The four vibronic absorption peaks at the shorter wavelength region are caused by the 9,10-diphenylanthracene moieties.[38−40] The peak maxima positions for the 9,10-diphenylanthracene units appear at 340, 360, 378, and 400 nm both for films and solutions regardless of the polymer structures.[40] Essentially, there are no changes in absorption maxima of the 9,10-diphenylanthracene (DPA) units for **P-1** and **P-2**. The peak positions for 9,10-diphenylanthracene (DPA) in 1,1,2,2-tetrachloroethane solution appear at 337, 355, 373, and 394, respectively. The absorption band maxima for this DPA moiety in the polymers are slightly red shifted compared with the absorption maxima of the corresponding DPA molecule by itself. This suggests that there is some interaction between the π-electrons in the main chain and the pendent groups. This interaction is also evidenced by a change in the extinction coefficient of the DPA band as exhibited by Figure 2a.

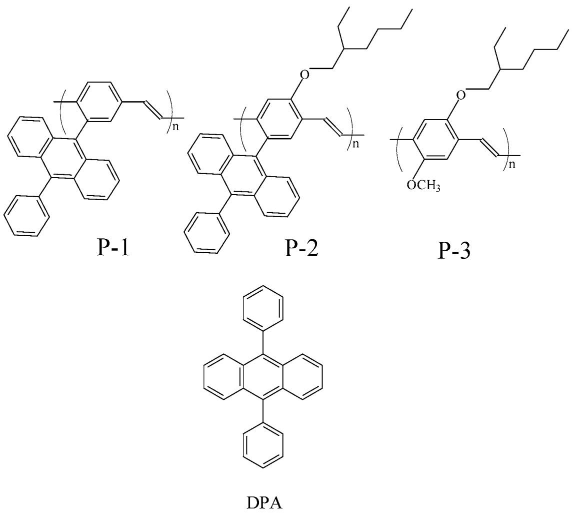


Figure 1. Chemical structures of **P-1**,**P-2**, and **Meh-PPV (P-3)**.

Figure 2b shows the one-photon excitation spectra obtained by monitoring the fluorescence at 500 nm for **P-1**, at 550 nm for **P-2**, and at 600 nm for **P-3**, respectively. For **P-1** and **P-2**, there are significant differences between the absorption and the excitation spectra. While in absorption, the peaks in the shorter

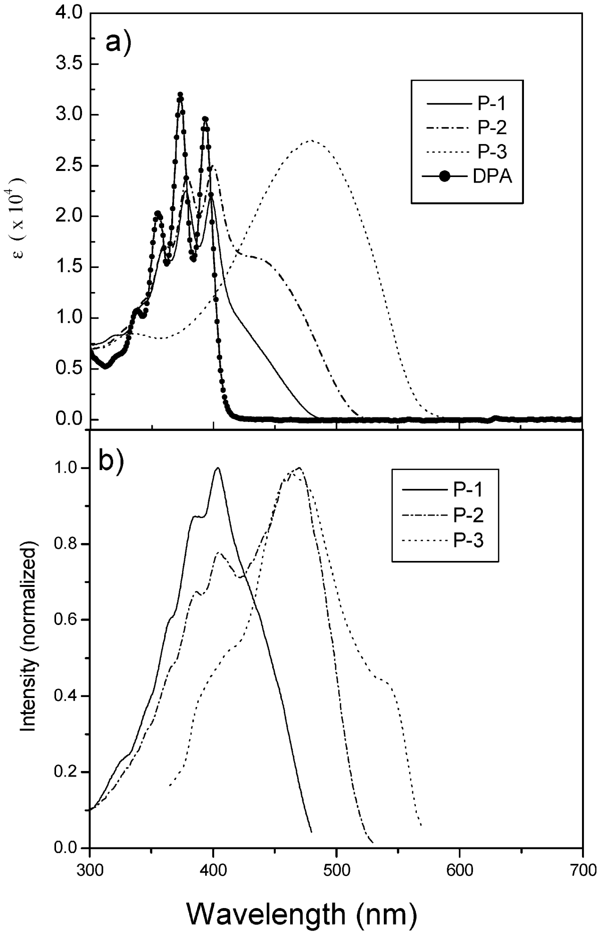


Figure 2. a) Absorption spectra of **P-1**, **P-2**, **P-3**, and 9,10-diphenylanthracene (**DPA**); b) one-photon excitation spectra of **P-1**, **P-2**, and **P**-3 (fluorescence monitored at 500 nm, 550 nm, and 600 nm for **P-1, P-2,** and **P-3,** respectively) in 1,1,2,2-tetrachloroethane. Concentration = 10^{-4} mol/L in repeating unit.

wavelength region derived from the pendent side chain dominate, the excitation spectra show that a more efficient excitation for emission is provided by absorption in the longer wavelength region derived from the main chain. For **P-3,** which does have a pendent chromophore, the absorption and the excitation peaks are closely matched.

The photoluminescence (PL) behaviors of these PPV derivatives were studied in 1,1,2,2-tetrachloroethane solution using the excitation wavelength of 405 nm (Figure 3a). 9,10-Diphenylanthracene (DPA) in 1,1,2,2- tetrachloroethane solution emits light in the spectral range 400−500 nm, with the peak of emission at 405 nm and a strong vibronic band at 428 nm. However, emissions of **P-1** and **2** start from about 450 nm. This emission has characteristics of PPV emission. This suggests complete energy transfer from the pendent phenylanthracene group to the PPV backbone from where the emission originates. Jin and co-workers[41] reported the steady-state and time-resolved PL spectra for the film of PPV derivatives using the excitation wavelength of 300−325 nm to photoexcite the side groups, phenylanthracene, to investigate the side-chain effect on the PL emission preferentially. According to their results, the PL spectra of PPV derivatives (**P-1**) carrying phenylanthracene as a pendent group are composed of well-resolved vibronic bands, being similar to the spectral features of PPV emission without interference by the pendent group and the energy-transfer process may occur from the pendent group to the PPV main chain. The PL spectrum of **P-2** shows red-shifted emission compared to **P-1**. The electron donating alkoxy substituents in **P-2** and Meh-PPV (**P-3**) produce this red shift as has been reported earlier for Meh-PPV.[42]

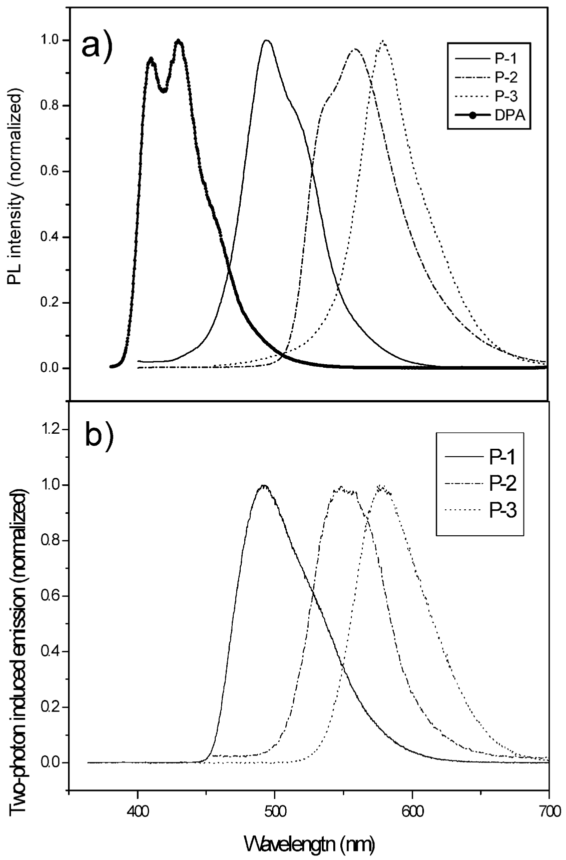


Figure 3. a) One-photon excited emission spectra of **P-1**, **P-2**, **P-3**, and 9,10-diphenylanthracene (DPA) (path length = 1 cm and OD < 0.01). and b) two-photon induced emission spectra of **P-1**, **P-2**, and **P-3** (path length of the cell is 0.1 cm) in 1,1,2,2-tetrachloroethane. Concentration = 10^{-4} mol/L in repeating unit.

Nonlinear Optical Properties of Polymer Solutions

Two-Photon Absorption Measurement. These PPV derivatives have strong linear absorption around 400−500 nm, but no absorption in the spectra ranging from 600 to 1100 nm. The feature at 825 nm is due to the exchange of the lamps in the spectrophotometer. Thus, upon irradiation with a laser at 800 nm, there should not be any linear (one-photon) absorption induced fluorescence emission. The energy of two infrared photons at 800 nm falls within the strong one-photon absorption band of these polymer solutions. Experimental measurements have shown that a strong frequency-upconverted fluorescence emission can be easily observed from the polymer solutions with an unfocused Q-switched near-IR laser beam at the wavelength range mentioned above. This indicates that a quite strong two-photon absorption process is occurring within the polymer samples. Here, we investigated the nonlinear (two-photon) absorption properties of the PPV derivatives using two different laser systems: a 8 ns, 810 nm dye laser pumped by a frequency-doubled Nd:YAG laser operating at 10 Hz repetition rate and a 135 fs, 796 nm, Ti:sapphire oscillator/amplifier laser operating at a 1 kHz repetition rate. The nonlinear absorption behavior of the chromophores **P-1**, **P-2, P-3**, and DPA were studied by measuring the transmission changes with the incident laser intensity. This was achieved by focusing the excitation beam in the sample cell using a ~20 cm focal length lens. The

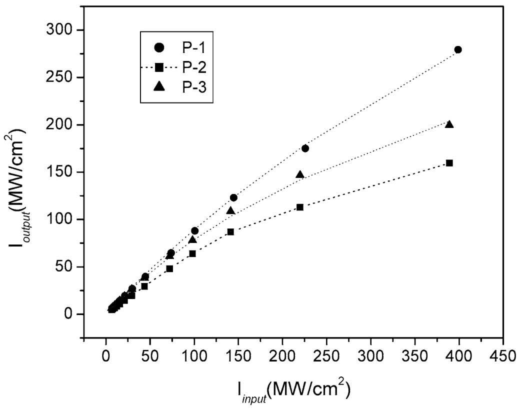


Figure 4. Nonlinear transmission data using a nanosecond laser (8 ns, 10 Hz, 810 nm) as the excitation source.

sample cell was a 1 cm long quartz cuvette filled with 0.02 mol/L of the PPV derivatives in 1,1,2,2-tetrachloroethane solutions. Then, the sample cell position was smoothly varied along the laser beam direction, so that the local incident intensity could be changed under a fixed incident pulse energy level (Z-scan technique). The transmitted light changes were monitored using a large area pyroelectric detector (30 nm diameter) placed at the far-field region (~30 cm far from the focusing lens).

The nonlinear (two-photon) absorption coefficient can be obtained by the analysis of the transmission changes with the incident irradiance using the propagation equation of light through a nonlinear optical material that presents two-photon absorption:

$$\frac{dI(z)}{dz} = -\alpha I(z) - \beta(I(z))^2 \qquad (1)$$

where $I(z)$ is the laser irradiance (intensity) along the position z, the propagation direction. The parameters α and β are the linear and two-photon absorption (TPA) coefficients, respectively. The parameter α is obtained from the linear absorption spectra of the samples and β is obtained by fitting the solution of eq 1 with the experimental data. The values of the TPA coefficients for the polymers studied here were calculated from the nonlinear transmission data obtained using nanosecond pulses and the Z-scan data obtained using femtosecond pulses. The TPA cross section is estimated from β using the following equation:

$$\sigma_{\mathrm{TPA}} = \beta/(N_{\mathrm{A}} d 10^{-3}) \qquad (2)$$

where N_{A} is the Avogadro number (6.02×10^{23}), d is the repeating unit concentration (mol/L), and σ_{TPA} is the two-photon absorption cross section. Figure 4 shows the nonlinear absorption results for **P-1**, **P-2**, and **P-3** using a 8 ns, 810 nm dye laser pumped by a frequency-doubled Nd:YAG laser operating at 10 Hz repetition rate as the source for nanosecond pulses. The leaser beam was focused with a $f = 20$ cm lens and passed through a 1 cm path quartz cuvette filled with the solution sample. DPA did not exhibit any significant two-photon absorption at this wavelength. Note that **P-2** presents a stronger nonlinear absorption. The same trend was observed in femtosecond Z-scan measurements, shown in Figure 5. Again, no significant two-photon absorption was observed for DPA at this wavelength. The depth of valley in the Z-scan is proportional to the nonlinear absorption coefficient of the respective samples and, for their equal concentration, they are proportional to the effective two-photon cross section. **P-2** is the material that presents the strongest nonlinear absorption at the wavelength of ~800 nm. The σ_{TPA} values measured in nanoseconds and femtoseconds are given Table 1. The σ_{TPA} values measured by using femtosecond laser pulses are roughly 2−3 orders of magnitude smaller than those measured by using nanosecond laser pulses.[43,44] Predominant excited state absorption in nanosecond excitation is cited as the reason for this difference in nanosecond and femtosecond measurements. A similar trend was found in a recent studies of new two-photon organic molecules.[45] Nevertheless, we can observe that **P-2** exhibits the best performance as a two-photon absorber in both nano- and femtosecond measurements. The two-photon cross section obtained from the sum-over-states approach [46] is given by

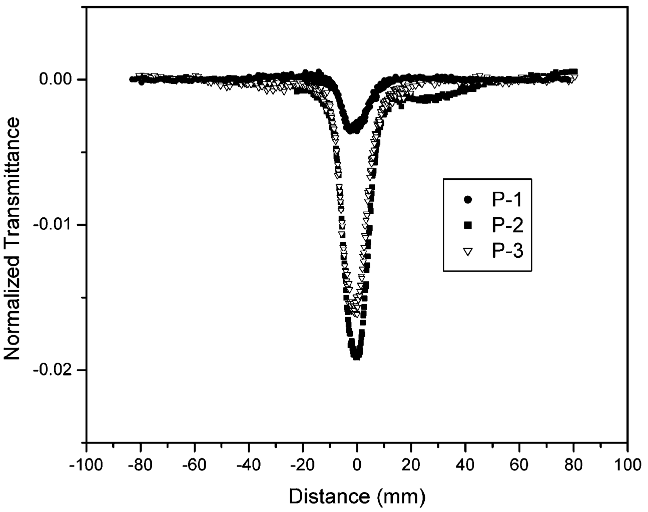


Figure 5. The Z-scan traces for **P-1**, **P-2**, and **P-3** of the equal concentration solutions in 1,1,2,2-tetrachloroethane (0.02 mol/L in repeating unit). The average pulse length is 135 fs, and the peak irradiance at the focal point is 50 GW/cm^2 at a wavelength of 796 nm.

TABLE 1: TPA Cross-Section Values Measured for P-1, P-2, and P-3 under Nanosecond Pulses at 810 nm and Femtosecond Pulses at 796 nm in 1,1,2,2-Tetrachloroethane Solution[a]

	P-1	**P-2**	**P-3**
solvent	TCE	TCE	TCE
concentration (mol/L)	0.02	0.02	0.02
wavelength (nm)	810 (796)	810 (796)	810 (796)
NLO absorption coefficient β (cm/GW)	0.297	1.665	1.101
σ_{TPA} (10^{-20} cm^4/GW)	11.9 (0.074)	66.6 (0.196)	44.0 (0.168)

[a] Values are femtosecond data.

$$\acute{o}_{02} \propto \frac{M_{01}{}^2 M_{12}{}^2}{(E_1 - \eta\grave{u})^2 \tilde{A}_{20}} \qquad (3)$$

where subscripts 0, 1, and 2 refer to levels S_0, S_1, and S_2. M_{ij} is the transition dipole moment from level i to level j, Γ_{02} is the damping factor, E_1 is the energy of S_1, and $h\omega$ is the excitation photon energy. Therefore, according to eq 3, there are basically two ways of increasing the TPA cross section: by increasing the transition dipole moments and by reducing the detuning between the first singlet excited state and the laser energy. Our results showed that **P-2** has the largest TPA cross section. However, this result reflects the TPA cross-section measurements only at one wavelength (~800 nm). To get more insight into the structure and two-photon absorption property relation, a measurement of the two-photon absorption spectrum needs to be obtained. This was accomplished by studying the two-photon excitation spectra as described below after a description of the two-photon excited fluorescence.

Two-Photon Excited Fluorescence Emission. Figure 3b shows the two-photon induced emission spectra of 1 mm path PPV derivative samples excited with the 800 nm laser beam. DPA exhibited only weak two-photon excited emission. Comparing Figure 3b to Figure 3a, one can see that the spectral profile of the emission bands of **P-1**, **P-2**, and **P-3** samples are basically the same for both one-photon and two-photon excitations. This indicates that the emissions in these polymers originate from the same singlet (S_1) in both one- and two-photon excitations.

Two-Photon Excitation Spectra. To obtain information on the two-photon absorption as a function of wavelength, the two-photon excitation spectra were obtained monitoring the two-photon upconverted fluorescence. A mode-locked, femtosecond, Ti:sapphire laser (Spectra-Physics, Tsunami) pumped by a DPSS laser (Spectra Physics, Millenia) was used for pulsed excitation. The pulse width was continuously monitored using an autocorrelator (NT&C, Germany). A spectrum analyzer (IST-rees) was used to monitor the wavelengths of excitation. The laser beam was focused onto the sample using a 5 cm focal length lens and the fluorescence spectra were collected using a fiber coupled monochromator (Holospeec from Kaiser Institute) and a CCD camera system (Princeton Instruments). The total fluorescence intensity collected for each sample at each wavelength was calculated as the area under the collected fluorescence spectra. The wavelength of the laser was tuned from 715 to 890 nm and the average power of excitation, the wavelength and the pulse width were monitored and the fluorescence spectra were recorded for each dye. By monitoring the fluorescence spectra using a spectrometer, we were able to monitor the emission spectra at different excitation wavelengths. In case of all the samples prepared here we found no change in the emission spectra with different two photon excitation wavelengths.

According to Xu and Webb,[47] the total fluorescence intensity is given by

$$\langle F(t)\rangle = \frac{1}{2}\phi\eta_2 C\sigma\frac{g_p}{f\tau}\frac{8n\langle P(t)\rangle^2}{\pi\lambda} \tag{4}$$

where $\langle F(t)\rangle$ is the total average fluorescence intensity collected, η_2 is the fluorescence quantum efficiency of the dye, and ϕ is the fluorescence collection efficiency of the dye; C is the concentration of the dye in solution and σ is the two photon excitation cross section; g_{p/f_τ} is the degree of second-order coherence (g_p depends only on pulse shape, which in this case is a hyperbolic-secant function, and has value of $g_p = 0.588$), n is the refractive index, and $\langle P(t)\rangle$ is the average excitation power. For one dye most of the parameters can be taken as a constant, reducing eq 4 to be

$$\langle F(t)\rangle \propto \sigma\frac{1}{\tau}\frac{\langle P(t)\rangle^2}{\lambda} \tag{5}$$

or

$$\sigma \propto \frac{1}{\langle P(t)\rangle^2}\lambda\tau\langle F(t)\rangle \tag{6}$$

Therefore, the collected fluorescence spectra were normalized with the above factor to get the fluorescence excitation spectra.

The obtained two-photon excitation spectra in terms of a plot of the normalized fluorescence efficiency are shown in Figure 6 for **P-1**, **P-2**, and **P-3**. Comparison of the spectra shows that **P-2** has a higher two-photon absorption at ~800 nm, resulting from the small detuning between the two-photon excitation wavelength and the energy of the first excited singlet, but **P-3** has a higher two-photon absorption at a longer wavelength.

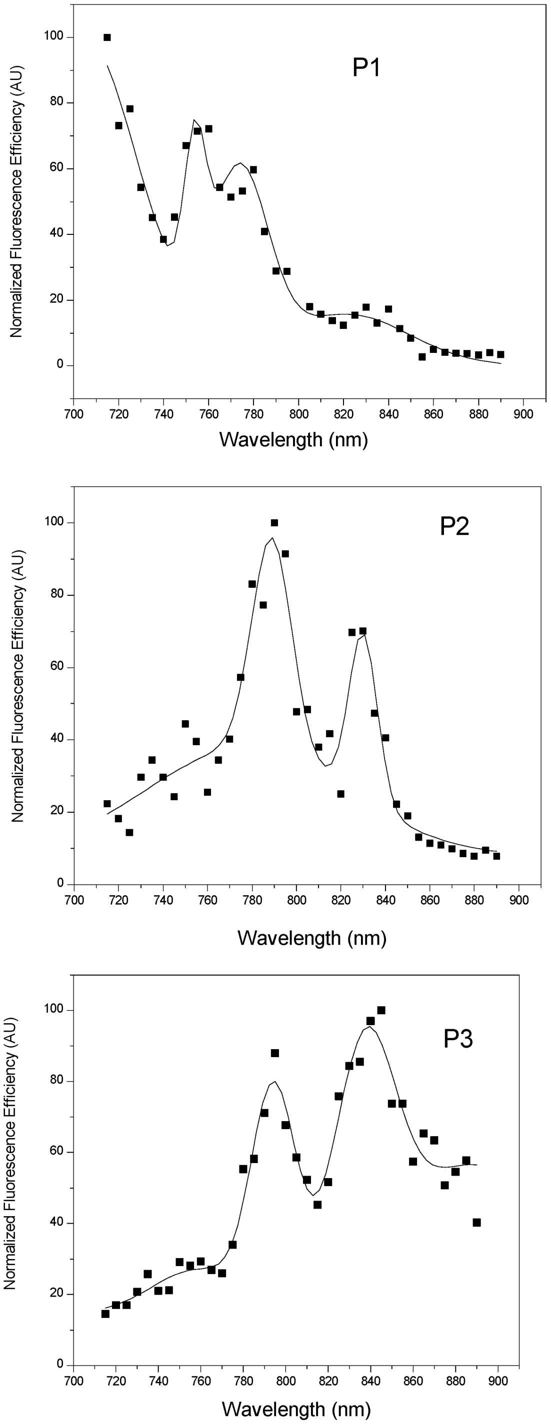


Figure 6. Normalized fluorescence efficiency as a function of wavelength of two-photon excitation.

Experimental Section

Characterization. The structure of the intermediates and polymers were verified by FT-IR (Bomen Michelson Series), and 1H NMR (Varian Gemini 300) spectroscopy and elemental analysis (Perkin-Elmer, Model 240 Elemental Analyzer). Melting points were determined using a Fisher-Johns melting point apparatus o perating at a rate of 30 °C/min. The purity of products was also deterimined by a combination of TLC on silica gel plates (Merck, silica gel 60 F254) with UV lamp (254 or 365 nm) and a visualization reagent. All optical characterizations were conducted using solutions of polymers in 1,1,2,2-tetrachoroethane. The UV−vis absorption and fluorescence studies were conducted with 10^{-4} M solutions in the concentration of the repeating unit using a Shimadzu, UV-3101PC spectrophotometer and a Shimadzu, RF5000U spectrofluorimeter. Relative molecular weights and molecular weight distributions of polymers were determined by gel permeation chromatography (GPC) using a Waters 510 instrument equipped with a 410 differential refractometer and photodiode array UV detector. Toluene was employed as eluent with a flow rate of 1.0 mL/min. Styragel was the column material and a calibration plot constructed with polystyrene standards. The thermal analysis of the polymers was performed in N2 atm on a differential scanning calorimeter (Metter DSC 821e) and also on a thermogravimetric analyzer (Metter TGA 50) at a heating rate of 10 °C /min.

Two-Photon Fluorescence Measurements. A Ti:sapphire laser (Tsunami from Spectra Physics) operating at 84 MHz repetition rate and 80 fs pulse duration tuned to ∼800 nm was used as the excitation source. The laser beam at an average power of 500 mW was focused on to the sample using an 5 cm focal length lens. The two-photon excited emission spectra was collected using a fiber-coupled spectrometer (Holospec from Kaiser Optical Systems, Inc.) attached with a CCD camera (Princeton Instruments).

Solution Characterization of Two-Photon Absorption Properties. Two-photon absorption cross section values of the three polymers in 2×10^{-2} M solution were measured with both nanosecond (810 nm) and femtosecond (796 nm) pulses. We have used direct nonlinear transmission measurement at ∼810 nm with ∼8 ns pulses from a Nd:YAG pumped dye laser at the intensity levels of several hundreds of megawatt per square centimeter. The experimental setup and data processing procedure are basically the same as those described in previous publications 46. Femtosecond Z-scan measurements were performed using the same solutions as for the nanosecond nonlinear transmission measurements. The Z-scan apparatus utilizing femtosecond pulses and the arrangement of the pump−probe experiment is described elsewhere (ref 43). The data analysis follows the same method as well. The laser system based on Ti:sapphire oscillator generated train (93 MHz) of 80 fs pulses at 796 nm central wavelength. Selected pulses were amplified in a Ti:sapphire regenerative amplifier using a chirped pulse amplification scheme. The final pulse energy was about 200 μJ and only a small fraction of that energy (below 1 μJ) was used in experiments at the wavelength of 796 nm. The pulse length of amplified pulses was checked with an autocorrelator and typically was about 131 fs.

Materials. All the compounds were purchased from Aldrich, TCI, or Fluka chemicals. Tetrahydrofuran (THF), *N*-bromosuccinimide (NBS), benzoyl peroxide (BPO), and 1,1,2,2-tetrachloroethane were purified by the method in ref 48. All other compounds were used as received.

Synthesis. *2-(9-Phenylanthracen-10-yl)-p-*xylene (***1***). 9-Bromo-10-phenylanthracene (15 g; 45 mmol) was dissolved in 150 mL of toulene containing 1.73 g of the tetrakis(triphenylphosphine)-palladium (0) catalyst. To this solution was added 7.84 g (58.5 mmol) of 2,5-dimethylphenyl boronic acid dissolved in 25 mL of ethanol and 45 mL of 2 M Na_2CO_3 solution. The mixture was refluxed for 48 h with vigorous stirring. The toluene layer was separated and toluene was removed by distillation, leaving behind a solid residue. The solid residue was thoroughly washed with methanol. The product was recrystallized from a mixture of methylene chloride and *n*-hexane (v/v = 1/5). The yield was 14.5 g (90%; mp = 176−178 °C). Anal. Calcd. (%) for $C_{28}H_{22}$: C, 93.81; H, 6.19. Found: C, 93.62; H, 6.35. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.98 (s, 3H), 2.48 (s, 3H), 7.3−7.85 (m, 16H). FT-IR (KBr, cm^{-1}): 3070 (aromatic C−H stretching), 2930 (aliphatic C−H stretching), 1450, 1610 (aromatic C=C stretching).

*2-(9-Phenylanthracen-10-yl)-1,4-bis(bromomethyl)benzene (**2**).* 2-(9-Phenyl- anthracen-10-yl)-*p*-xylene (**1**) (7 g; 19.5 mmol), *N*-bromosuccinimide (7.6 g; 43 mmol), and benzoyl peroxide (0.47 g; 1.95 mmol) were dissolved in 150 mL of CCl_4. The mixture was refluxed under a N_2 atmosphere for 4 h. The succinimide formed was removed by filteration, and the CCl_4 in the filtrate was evaporated using a rotatory evaporator. The residue was recrystallized from a mixture of *n*-hexane and ethyl acetate (v/v = 5/1). The yield was 4.2 g (42%; mp = 152 °C). Anal. Calcd. (%) for $C_{28}H_{20}Br_2$: C, 65.16; H, 3.90; Br, 30.95. Found: C, 65.62; H, 3.94. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 4.16 (s, 2H), 4.55 (s, 2H), 7.35−7.8 (m, 16H). FT-IR (KBr, cm^{-1}): 3024 (aromatic C−H stretching), 2930 (aliphatic C−H stretching), 1450, 1610 (aromatic C=C stretching), 1162 (C−Br bending), 704 (C−Br stretching).

*2,5-Dimethyl-4-(9-phenylanthracen-10-yl)anisole (**3**).* 2,5-Dimethyl-4-bromo- anisole (19 g; 90 mmol) was dissolved in 150 mL of dry THF containing 2.2 g (91 mmol) of magnesium. The reaction mixture was refluxed under nitrogen atmosphere for 4h. The reaction mixture was cooled to 0 °C, and to this solution was added 26.7 g (80 mmol) of 9-bromo-10-phenylanthracene in 100 mL of dry THF and 0.2 g (3 mmol) of $NiCl_2 \cdot 2PPh_3$ catalyst in ice bath. The reaction mixture was heated to 60 °C under N_2 atmosphere and held at that temperature for 12 h. The mixture was cooled to room temperature and poured into 500 mL of 1 M HCl solution. After extraction with ethyl acetate, the solvent was removed by distillation. The residue was purified by column (silica gel) chromatography using *n*-hexane as eluent. The yield was 22 g (72%; mp = 198−200 °C). Anal. Calcd. (%) for $C_{29}H_{24}O$: C, 89.66; H, 6.23. Found: C, 89.72; H, 6.22. 1H NMR (300 MHz, $CDCl_3$, ppm): 1.91 (s, 3H), 2.27 (s, 3H), 3.97(s, 3H), 6.92(s, H), 7.06 (s, H), 7.30−7.68 (m, 13H). FT-IR (KBr, cm^{-1}): 3061 (aromatic C−H stretching), 2927 (aliphatic C−H stretching), 1609, 1502 (aromatic C=C stretching), 1247, 1020 (C−O−C stretching).

*2,5-Dimethyl-4-(9-phenylanthracen-10-yl)phenol (**4**).* Hydrobromic acid (48%, 40 mL) was added slowly with stirring to solution of compound (**3**) (16 g; 40 mmol) dissolved in 300 mL of a mixture of acetic acid and trifluoroacetic acid (v/v = 5/1). The reaction mixture was refluxed for 3 days under a nitrogen atmosphere during which period the whole mixture became homogeneous. After the mixture was cooled to room temperature, the precipitate formed was collected on a filter and washed thoroughly with a mixture of distilled water and ethanol (v/v = 1/1). The product was recrystallized from a mixture of *n*-hexane and ethyl acetate (v/v = 9/1). The yield was 12 g (84%; mp = 193 °C). Anal. Calcd. (%) for $C_{28}H_{22}O$: C, 89.81; H, 5.92. Found: C, 89.94; H, 5.92. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.85 (s, 3H), 2.31 (s, 3H), 4.89(s, H), 6.87 (s, H), 7.04 (s, H), 7.30−7.62 (m, 13H). FT-IR (KBr, cm-1): 3700−3100 (O−H stretching), 3058 (armatic C−H stretching), 2961 (aliphatic C−H stretching), 1612, 1507 (aromatic C=C stretching).

*2-Ethylhexyloxy-4-(9-phenylanthracen-10-yl)-2,5-dimethylbenzene (**5**).* Compound **4** (15 g; 43 mmol), 10 g (51.6 mmol) of 2-ethylhexyl bromide, and 2.8 g (51.6 mmol) of KOH were dissolved in 150 mL of ethanol. The mixture was refluxed for 24 h under a nitrogen atmosphere. The insoluble was removed by filtration. Solvent in the filtrate was removed by distillation using a rotary evaporator. The crude product was recrystallized from ethanol. The yield was 16 g (82%; mp = 139 °C). Anal. Calcd. (%) for $C_{36}H_{38}O$: C, 88.84; H, 7.87. Found: C, 88.67; H, 7.89. 1H NMR (300 MHz, $CDCl_3$, ppm): 0.94−1.05 (m, 6H), 1.41 (m, 4H), 1.51−1.68(m, 4H), 1.84 (m, H), 1.90 (s, 3H), 2.28 (s, 3H), 4.01 (d, 2H), 6.90 (s, H), 7.05 (s, H), 7.29−7.71(m, 13H). FT-IR (KBr, cm^{-1}): 3062 (aromatic C−H stretching), 2927 (aliphatic C−H stretching), 1606, 1502 (aromatic C═C stretching), 1247, 1020 (C−O−C stretching).

*2-Ethylhexyloxy-5-(9-phenylanthracen-10-yl)-1,4-bis(bromomethyl)benzene (**6**).* Compound **5** (5 g; 11 mmol), *N*-bromosuccinimide (4.5 g; 25 mmol), and benzoyl peroxide (0.27 g; 1 mmol) were dissolved in 150 mL of CCl_4. The mixture was refluxed under a N_2 atmosphere for 4 h. The succinimide formed was removed by filtration, and the CCl_4 in the filtrate was evaporated using a rotatory evaporator. The residue was purified by column (silica gel) chromatography and a mixture of *n*-hexane and ethyl acetate (v/v = 5/1). The yield was 2.8 g (42%; mp = 129 °C). Anal. Calcd. (%) for $C_{36}H_{36}Br_2O$: C, 67.27; H, 5.64. Found: C, 67.31; H, 5.59. 1H NMR (300 MHz, $CDCl_3$, ppm): 0.70−1.05 (m, 6H), 1.42 (m, 4H), 1.52−1.74 (m, 4H), 1.89 (m, H), 4.13 (s, 2H), 4.21 (d, 2H), 4.62 (s, 2H), 7.20−7.80 (m, 15H). FT-IR (KBr, cm^{-1}): 3058 (aromatic C−H stretching), 2921,2857 (aliphatic C−H stretching), 1604, 1507 (aromatic C═C stretching), 1210, 1018 (C−O−C stretching), 696 (C−Br stretching).

*Poly[2-(9-phenylanthracen-10-yl)-1,4-phenylenevinylene] (**P-1**).* A solution of potassium *tert*-butoxide (1.3 g, 12 mmol) in THF (12 mL) was added over 5 min at room temperature to a stirred solution of 2-(9-phenylanthracen-10-yl)1,4-bis(bromomethyl)benzene (1.0 g; 20 mmol) in a mixture of THF (25 mL) and *p*-xylene (25 mL) under nitrogen atmosphere. The reaction mixture was stirred for 6 h at room temperature and for 1 h at 60 °C. The yellowish solution was added dropwise to stirred cold methanol (300 mL), and the resulting mixture was stirred for 1 h. After filtration, the solid was washed with methanol, dried under vacuum overnight, then redissolved in 1,1,2,2-tetrachloroethane (30 mL) and precipitated twice again into methanol (300 mL). The collected yellowish polymer (0.3 g; 42%) was dried under vacuum. Anal. Calcd. (%) for $C_{28}H_{20}$: C, 94.35; H, 5.65. Found: C, 93.62; H, 5.35. 1H NMR (300 MHz, $CDCl_2CDCl_2$, ppm): 6.15−6.42 (broad, 2H), 7.17−7.69 (m, 18H). FT-IR (KBr, cm^{-1}): 3046 (aromatic C−H stretching), 1588,1517 (aromatic C═C stretching), 959 (trans = C−H out-of-plane stretching).

*Poly[2-(2-ethylhexyloxy)-5-(9-phenylanthracen-10-yl)-1,4-phenylenevinylene] (**P-2**).* **P-2** was prepared in 44% yield from 2-(2-ethylhexyloxy)-5-(9-phenylanthracen-10-yl)-1,4-bis(bromomethyl)benzene (**6**) (1 g; 1.7 mmol) in THF (50 mL). Anal. Calcd. (%) for $C_{36}H_{34}O$: C, 89.58; H, 7.10. Found: C, 88.97; H, 7.16. 1H NMR (300 MHz, $CDCl_2CDCl_2$, ppm): 0.51−1.85 (m, 15H), 3.96 (d, 2H), 6.34−6.59 (d, 2H), 6.81−7.79 (m, 15H). FT-IR (KBr, cm-1): 3053 (aromatic C−H stretching), 2923, 2859 (aliphatic C−H stretching), 1602, 1504 (aromatic C═C stretching), 1219, 1020 (C−O−C stretching), 965 (trans = C−H out-of-plane stretching).

Conclusion

We have synthesized new PPV derivatives carrying phenylanthracene and both phenylanthracene and 2-ethylhexyloxy substituents as described by Gilch and Wheelwright.[37] These polymers were highly soluble in common organic solvents.

These PPV derivatives exhibited strong two-photon pumped up-conversion emission when excited by both nanosecond and femtosecond laser pulses. We observed that **P-2** having both the phenylanthracene and 2-ethylhexyloxy substiuent as pendent groups revealed the best performance as a two-photon absorber.

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