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Synthesis, One- and Two-Photon Properties of Poly[9,10-bis(3,4-bis(2-ethylhexyl-oxy)phenyl)-2,6-anthracenevinylene-*alt*-*N*-octyl-3,6-/2,7-carbazolevinylene]

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ABSTRACT: The synthesis, one- and two-photon absorption (TPA) and emission properties of two novel 2,6-anthracenevinylene-based copolymers, poly[9,10-bis(3,4-bis(2-ethylhexyloxy)phenyl)-2,6-anthracenevinylene-*alt*-*N*-octyl-3,6-carbazolevinylene] (**P1**) and poly[9,10-bis(3,4-bis(2-ethylhexyloxy)phenyl)-2,6-anthracenevinylene-*alt*-*N*-octyl-2,7-carbazolevinylene] (**P2**) were reported. The as-synthesized polymers have the number-average molecular weights of 1.56×10^4 for **P1** and 1.85×10^4 g mol⁻¹ for **P2** and are readily soluble in common organic solvents. They emit strong bluish-green one- and two-photon excitation fluorescence in dilute toluene solution ($\Phi_{P1} = 0.85$, $\Phi_{P2} = 0.78$, $\lambda_{em}(P1) = 491$ nm, $\lambda_{em}(P2) = 483$ nm). The maximal TPA cross-sections of **P1**

and **P2** measured by the two-photon-induced fluorescence method using femtosecond laser pulses in toluene are 840 and 490 GM per repeating unit, respectively, which are obviously larger than that (210 GM) of poly[9,10-bis-(3,4-bis(2-ethylhexyloxy)phenyl)-2,6-anthracenevinylene], indicating that the poly(2,6-anthracenevinylene) derivatives with large TPA cross-sections can be obtained by inserting electron-donating moieties into the polymer backbone. © 2009 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 48: 463–470, 2010

KEYWORDS: 2,6-anthracene-vinylene-based polymers; conjugated polymers; NLO; photophysics; two-photon absorption

INTRODUCTION Two-photon absorption (TPA) has become of great interest in the photosciences owing to potential applications in three-dimensional (3D) fluorescence imaging,¹ optical power limitation,² lasing up-conversion,³ 3D optical data storage,⁴ 3D micro-fabrication,⁵ and photodynamic therapy.⁶ A variety of compounds exhibiting TPA properties, including donor-acceptor-donor (D-A-D) type molecules, donor- π -bridge-acceptor (D- π -A) type molecules, donor- π -bridge-donor (D- π -D) type molecules, macrocycles, dendrimers, polymers, and multibranched compounds have been synthesized and their structure-property relationships have been investigated.⁷ The results of these studies reveal that TPA cross-sections (δ) increases with the donor/acceptor strength, conjugation length, molecular dimensionality, and the planarity of the π -center.

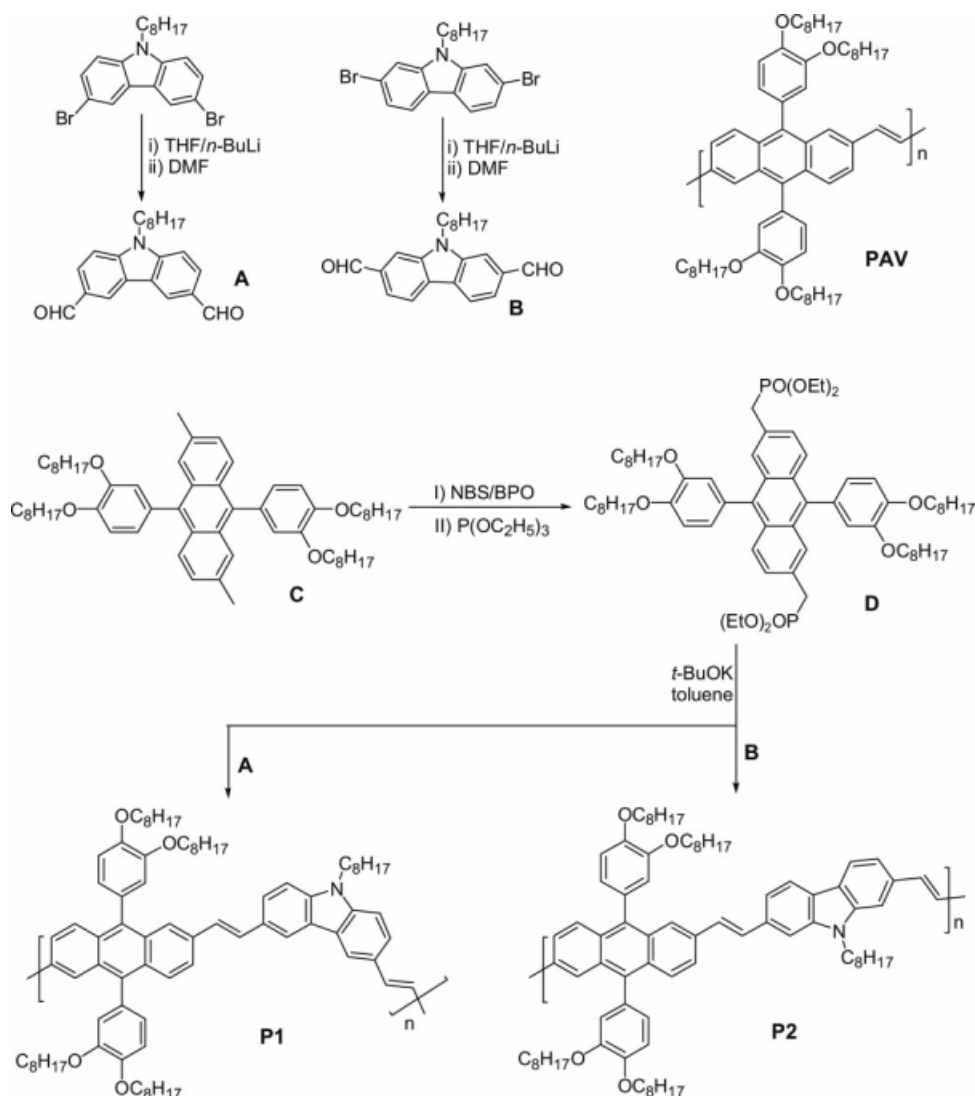
In electronic, photonic, and optoelectronic fields, two types of conjugated materials, small molecules and polymers, have been used. For some practical applications, small molecular materials have to be incorporated into the host polymer for avoiding aggregation at high concentration,^{8,9} and their disperse concentration in the host polymer matrix is limited by the phase separation. Since the higher degrees of conjugation could enhance δ and the low aggregations could allow higher concentration of the absorptive and fluorescent centers, the

conjugated polymers have become the targets of TPA interest.¹⁰ However, in comparison with extensively studied small molecular TPA chromophores, the conjugated polymers with large δ are still scarce at present.^{7,10–15} Although most typical conjugated polymers, such as ladder-type poly(*p*-phenylene),¹¹ polyfluorene,¹² poly(*p*-phenyleneethynylene),¹³ poly[1,6-bis(3,6-dihexadecyl-*N*-carbazolyl)-2,4-hexadiyne],¹⁴ poly(*p*-phenylenevinylene)s,¹⁵ have been studied to show $\delta > 10,000$ GM per repeating unit in nanosecond laser pulses, the δ values measured by using nanosecond pulses are roughly two to three orders of magnitude larger than those measured by using femtosecond pulses because of the existence of excited state absorption in nanosecond laser excitation.^{7(a),15(b)} The real δ for those traditional conjugated polymers are rather low. Therefore, there is still a considerable need for polymeric chromophores exhibiting large δ in femtosecond laser pulses.

Recently, to obtain the macromolecules with large δ and reduced aggregation, some hyperbranched polymers¹⁶ and dendrimers¹⁷ containing TPA-active units have been synthesized and shown the maximal δ up to 600 GM per repeating unit. Jen and coworkers have reported the synthesis and metal ion sensing properties of poly[(2,5-bis(*p*-di-*n*-butylaminostyryl)benzene-1,4-diyl)-*alt*-(fluorene-2,7-diyl)] with δ up

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SCHEME 1 Synthetic routes and chemical structures of **P1** and **P2**.

to 1000 GM.¹⁸ These results imply that the polymers exhibiting large δ could be constructed by employing molecular chromophores with large δ as building blocks or repeating units. In this work, we design and synthesize two novel donor-containing poly(2,6-anthracenevinylene)-based derivatives (**P1** and **P2**) by Wittig-Homer reaction between 9,10-bis(3,4-bis(2-ethylhexyloxy)phenyl)-2,6-bis(diethylphosphorylmethyl)anthracene and *N*-octyl-3,6/2,7-diformylcarbazole (Scheme 1). The incorporation of 2,7- and 3,6-carbazole can endow polymer backbone with different donor strength and conjugation length to investigate their one- and two-photon properties. Although the donor-containing conjugated polymers have been used in electroluminescence, photovoltaic cell, photoluminescence, and thin film transistor,¹⁹ their TPA properties have rarely been investigated. On the other hand, to the best of our knowledge, although various anthracene-based polymers and oligomers, such as poly(2,6-anthrylene), poly(9,10-anthrylene), poly(9,10-anthracenevinylene), and their derivatives, have been extensively reported,²⁰ poly(2,6-anthracenevinylene)s and 2,6-anthracenevinylene-containing

polymers are very scarce at present because of their synthetic inaccessibility before.²¹ The 2,6 attachment of the vinylene linkage on the anthryl ring could provide novel structures and properties such as the stronger fluorescence and larger δ compared with the 9,10 attachment under the D- π -D motif.²² Very recently, we have developed a synthetic route to high solubility and high-molecular weight of poly(9,10-diphenyl-2,6-anthracenevinylene)s.^{21(b,c)} We now report the synthesis of donor-containing poly(9,10-diphenyl-2,6-anthracenevinylene)-based copolymers **P1** and **P2** and their large TPA cross-sections in femtosecond laser pulses. For the sake of comparison, poly[9,10-bis(3,4-bis(2-ethylhexyloxy)phenyl)-2,6-anthracenevinylene] (**PAV**) is also included.

EXPERIMENTAL

Materials

2,6-Dimethyl-9,10-bis(3,4-bis(2-ethylhexyloxy)phenyl)anthracene (**C**), **PAV**, *p*-(*N,N*-dihexyl-amino)benzaldehyde were available from previous works.^{21(c),22(a)} *N*-Octyl-3,6-dibromo-

carbazole and *N*-octyl-2,7-dibromocarbazole were supplied by professor Bo's group.²³ All the chemicals were purchased from Aldrich Chemical Co. Toluene, benzene, and tetrahydrofuran were distilled over metallic sodium before use. Other solvents and reagents were analytical grade and were used as received, unless otherwise claimed.

Measurements

¹H and ¹³C NMR spectra were recorded in CDCl₃ on a JEOL JNM-LA-300 (300 MHz) and 125-MHz AVANCE 500 (Bruker) spectrometer, respectively. Molecular weights were determined using gel permeation chromatography (GPC, Waters 1515 HPLC) equipped with Styragel columns and using THF as an eluent with polystyrene standards. The elemental analysis was performed on Perkin-Elmer 2400. The fluorescence quantum yield Φ_f was determined in toluene at room temperature by using quinine in 0.5 M H₂SO₄ as the reference. UV-vis absorption spectra were obtained on a Cary500 spectrophotometer. Fluorescence measurements were carried out on an Aminco Bowman series 2 luminescence spectrometer. The absorption maximum of the compound was used as the excitation wavelength for the PL measurement.

The TPA cross-section of the compounds was measured with the two-photon-induced fluorescence method by using the femtosecond laser pulses as described.²⁴ The excitation light source was a mode-locked Ti:sapphire fs laser (Spectra-Physics, Tsunami 3941, 700–910 nm, 80 MHz, <120 fs), which was pumped by a compact cw prolite diode laser (Spectra-physics, Millennia Pro 5S). The fluorescence signal was recorded by a spectrofluorometer (Ocean Optics, USB2000). Samples were dissolved in toluene at concentrations of 1.0×10^{-4} M in repeating unit and the two-photon induced fluorescence intensity was measured at 700–900 nm by using fluorescein (1.1×10^{-4} M in water, pH = 11) as the reference, and the two-photon properties of fluorescein have been well characterized in the literature.²⁵ The intensities of the two-photon induced fluorescence spectra of the reference and sample under the same measurement conditions were determined and compared (input power 100 mW, which is among the linear dependence of fluorescence intensity on the square of the excitation intensity, Fig. 3). The TPA cross-section of sample δ_s , measured by using the two-photon-induced fluorescence measurement technique, can be calculated by using the equation: $\delta_s = [(S_s \Phi_s c_r) / (S_r \Phi_r c_s)] \delta_r$, where the subscripts s and r stand for the sample and reference molecules, respectively.²⁴ S is the integral area of the two-photon fluorescence, Φ is the fluorescence quantum yield, and c is the number density of the molecules in solution. δ_r is the TPA cross-section of the reference molecule.

Synthesis of Monomers

N-Octyl-3,6-diformylcarbazole (A)

1.6 mL of *n*-Butyllithium (2.85 M in hexane, 4.6 mmol) was slowly added to a solution of *N*-octyl-3,6-dibromocarbazole (0.92 g, 2.1 mmol) in anhydrous THF (20 mL) at -78°C under nitrogen by using a syringe. The mixture was stirred at that temperature for 1 h and then 1 mL of anhydrous

DMF was slowly added. The resulting mixture was stirred 1 h at -78°C and for 5 h at room temperature. After quenching with water, the mixture was extracted with dichloromethane and solvent was evaporated off. The crude product was purified by column chromatography on silica gel using ethyl acetate/hexane (1/10) as the eluent to afford 0.45 g of a yellow solid (yield: 64%), mp 102–104 $^\circ\text{C}$.

¹H NMR (300 MHz, CDCl₃): δ 10.13 (s, 2H), 8.66 (s, 2H), 8.08 (d, $J = 9.0$ Hz, 2H), 7.54 (d, $J = 9.0$ Hz, 2H), 4.38 (t, $J = 7.5$ Hz, 2H), 1.91 (m, 2H), 1.26 (m, 10H), 0.85 ppm (t, $J = 6.0$ Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 192.404, 141.723, 135.131, 126.851, 121.790, 121.405, 110.245, 43.614, 31.706, 29.690, 29.280, 29.111, 27.215, 22.556, 14.031. ELEM. ANAL.: Calcd (%) for C₂₂H₂₅NO₂: C, 78.77; H, 7.51; N, 4.18; O, 9.54. Found: C, 78.66; H, 7.57; N, 4.24.

N-Octyl-2,7-diformylcarbazole (B)

Synthesized by the same procedure as described for *N*-octyl-3,6-diformylcarbazole except that *N*-octyl-2,7-dibromocarbazole was used. A white solid of 0.39 g was obtained (yield: 56%), mp 131–133 $^\circ\text{C}$

¹H NMR (300 MHz, CDCl₃): δ 10.19 (s, 2H), 8.28 (d, $J = 9.0$ Hz, 2H), 8.00 (s, 2H), 7.80 (d, $J = 9.0$ Hz, 2H), 4.43 (t, $J = 7.5$ Hz, 2H), 1.91 (m, 2H), 1.27 (m, 10H), 0.85 ppm (t, $J = 6.0$ Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 191.499, 144.752, 129.609, 127.807, 124.251, 123.230, 109.760, 43.797, 31.684, 29.230, 29.073, 28.901, 27.176, 22.542, 14.024. ELEM. ANAL.: Calcd (%) for C₂₂H₂₅NO₂: C, 78.77; H, 7.51; N, 4.18; O, 9.54. Found: C, 78.71; H, 7.55; N, 4.21.

2,6-Bis(diethylphosphorylmethyl)-9,10-bis(3,4-bis(2-ethylhexyloxy)phenyl)anthracene (D)

A mixture of 2,6-dimethyl-9,10-bis(3,4-bis(2-ethylhexyloxy)phenyl)anthracene (C) (1.1 g, 1.3 mmol), NBS (0.52 g, 2.92 mmol), and benzoyl peroxide (27 mg, 0.11 mmol) in anhydrous benzene (40 mL) was refluxed for 4 h. The suspension solid was filtered off and the solvent was removed by evaporation under reduced pressure. The residue dried in vacuum was added triethyl phosphate (30 mL) to be refluxed for 12 h. The excessive triethyl phosphate was distilled out by reduced pressure and the residue was purified by column chromatography on silica gel using ethyl acetate/CH₂Cl₂ (1:2) as the eluent to afford 0.88 g of white solid (yield: 61%), mp 61–63 $^\circ\text{C}$.

¹H NMR (300 MHz, CDCl₃): δ 7.70 (d, $J = 9.0$ Hz, 2H), 7.58 (d, $J = 3.0$ Hz, 2H), 7.32 (d, $J = 9.0$ Hz, 2H), 7.08 (dd, $J = 9.0$ Hz, 3.0 Hz, 2H), 6.93 (m, 4H), 3.99 (m, 12H), 3.83 (m, 4H), 3.20 (d, $J = 21$ Hz, 4H), 1.86 (m, 2H), 1.77 (m, 2H), 1.28–1.70 (m, 32H), 1.20 (t, $J = 7.5$ Hz, 12H), 0.88–1.05 ppm (m, 24H). ¹³C NMR (125 MHz, CDCl₃): δ 150.329, 148.666, 131.486, 130.806, 130.276, 128.845, 128.658, 128.413, 123.164, 122.839, 116.539, 114.778, 112.546, 71.797, 71.582, 62.401, 39.436, 34.893, 33.782, 30.501, 29.054, 23.829, 23.023, 16.416, 14.048, 11.110. ELEM. ANAL.: Calcd (%) for C₆₈H₁₀₄O₁₀P₂: C, 71.42; H, 9.17; O, 13.99; P, 5.42. Found: C, 71.38; H, 9.26.

TABLE 1 One- and Two-Photon Properties of **PAV**, **P1**, and **P2** in Toluene

Cpd	$M_n \cdot 10^{-4}$ (PDI)	λ_{\max}^a	λ_{fl}^b	$\Delta\tilde{\nu}^c$	Φ^d	λ_{TPA}^e	δ_{\max}^f
PAV	3.22 (3.37)	346, 446	496	2,210	0.50	790	210
P1	1.56 (2.04)	353, 419, 445	491	2,100	0.85	800	840
P2	1.85 (2.71)	354, 414, 437	483	2,180	0.78	810	490

^a The peak wavelength in the one-photon absorption spectra in nanometer (nm).

^b Peak wavelength of the one-photon fluorescence spectra in nanometer (nm).

^c Stokes shift in cm^{-1} .

^d Fluorescence quantum yield.

^e Peak wavelength of the two-photon absorption spectra in nanometer (nm).

^f The peak TPA cross-section in $10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$ (GM).

Polymerization

Poly[(9,10-bis(3,4-bis(2-ethylhexyloxy)phenyl)-2,6-anthracenevinylene)-alt-(9-oct-yl-carbazole-3,6-diyl)] (P1)

A solution of *N*-octyl-3,6-diformylcarbazole (**A**) (0.067 g, 0.20 mmol) and 2,6-bis(diethylphosphorylmethyl)-9,10-bis(3,4-bis(2-ethylhexyloxy)phenyl)-anthracene (**D**) (0.225 g, 0.20 mmol) in anhydrous toluene (10 mL) was degassed and then stirred for 5 min at 80 °C under nitrogen. *t*-BuOK (0.11 g, 0.96 mmol) was added in portions and then stirred 3 h at 100 °C. *p*-Diethylaminobenzaldehyde (12 mg, 41 μmol) was added and then reacted another 1 h. The mixture was poured into 100 mL of methanol to precipitate the polymer. The collected solid was dissolved into chloroform and filtered through a short pad of silica gel column. The filtrate was concentrated to ~ 10 mL and precipitated into stirred ethanol (50 mL). The formed precipitate was collected and dried under vacuum to afford **P1** as a yellow solid. 0.17 g (yield: 72%).

¹H NMR (300 MHz, CDCl_3): δ 8.31 (b, 2H), 8.04 (b, 2H), 7.73 (b, 4H), 7.45 (m, 2H), 7.32 (m, 2H), 7.18 (b, 6H), 7.04 (b, 4H), 4.31 (b, 2H), 3.95 (m, 8H), 1.95 (m, 6H), 1.27–1.61 (m, 42H), 0.91 ppm (m, 27H). ELEM. ANAL: Calcd (%) for $[\text{C}_{82}\text{H}_{107}\text{NO}_4]_n$: C, 84.12; H, 9.21; N, 1.20, O, 5.47. Found: C, 84.83; H, 9.13; N, 1.17.

Poly[(9,10-bis(3,4-bis(2-ethylhexyloxy)phenyl)-2,6-anthracenevinylene)-alt-(9-oct-yl-carbazole-2,7-diyl)] (P2)

Synthesized by the same procedure as described for **P1** except that *N*-octyl-2,7-diformylcarbazole (**B**) was used. **P2** was also a yellow solid. 0.15 g (yield: 64%).

¹H NMR (500 MHz, CDCl_3): δ 8.16 (b, 2H), 7.96 (b, 2H), 7.77 (b, 4H), 7.48 (m, 3H), 7.31 (m, 3H), 7.15–7.25 (m, 6H), 7.02 (b, 2H), 4.38 (b, 2H), 3.92 (m, 8H), 1.91 (b, 6H), 1.25–1.60 (m, 42H), 0.93 ppm (m, 27H). ELEM. ANAL: Calcd (%) for $[\text{C}_{82}\text{H}_{107}\text{NO}_4]_n$: C, 84.12; H, 9.21; N, 1.20, O, 5.47. Found: C, 83.84; H, 9.30; N, 1.22.

RESULTS AND DISCUSSION

Synthesis and Characterization

The synthesis and chemical structures of the copolymers **P1** and **P2** are shown in Scheme 1. *N*-Octyl-3,6-dibromocarbazole and *N*-octyl-2,7-dibromocarbazole are supplied by Bo's group.²³ 2,6-Dimethyl-9,10-bis(3,4-bis(2-ethylhexyloxy)phenyl)-anthracene (**C**) and **PAV** are from a previous study.^{21(c)} To

prepare *N*-octyl-3,6-diformylcarbazole (**A**) and *N*-octyl-2,7-diformylcarbazole (**B**), the corresponding dibromo-carbazoles were treated with *n*-butyllithium in anhydrous THF and then quenched by *N,N*-dimethylformamide. The radical-initiated bromination of **C** with NBS in anhydrous benzene followed by the treatment with $\text{P}(\text{OC}_2\text{H}_5)_3$ to afford 2,6-bis(di-ethylphosphorylmethyl)-9,10-bis(3,4-bis(2-ethylhexyloxy)phenyl)anthracene (**D**). All the intermediates were purified by column chromatography on silica gel and characterized by ¹H NMR and ¹³C NMR spectroscopy and elemental analysis. It has been shown that the Wittig–Hornor route produces polymers of well-defined structure, which are practically all trans vinylene bonds and simplify the structures.²⁶ Therefore, the Wittig–Hornor coupling between 2,6-bis(diethylphosphorylmethyl)anthracene (**D**) and the corresponding diformylcarbazole (**A** and **B**) was chosen to synthesize the copolymers **P1** and **P2**.

The as-synthesized **P1** and **P2** are readily soluble in common organic solvents, such as toluene, chloroform, dichloromethane, and tetrahydrofuran with the solubility > 20 mg mL^{-1} . We attribute the good solubility of the polymers to the presence of plenty of flexible side chains, which minimize polymer interchain interactions. We employed GPC using THF as the eluent and calibrating against polystyrene standards to determine the molecular weight of the polymers. **P1** and **P2** possess the number-average molecular weights (M_n) of $\sim 1.56 \times 10^4$ and $1.85 \times 10^4 \text{ g mol}^{-1}$, and the polydispersity indices of 2.04 and 2.71, respectively. The average numbers of repeating units of the as-synthesized polymers are estimated to be ~ 13 –15. Although the M_n values might be overestimated as observed in other conjugated polymers,²⁷ the as-synthesized polymers are readily film-forming by spin-coating their solutions (the optoelectronic properties in film states is under investigation).

Linear Optical Properties of Polymer Solutions

The photophysical properties of **P1** and **P2** are investigated in dilute toluene solutions. For the sake of comparison, homopolymer **PAV**^{21(b)} is also included. The normalized solution absorption and fluorescence spectra of **P1**, **P2**, and **PAV** are depicted in Figures 1 and 2, respectively. The corresponding photophysical data are summarized in Table 1. The incorporation of carbazole unit into the polymer backbone increases the relative intensities of the longest wavelength absorption band (Fig. 1). Moreover, both the emission

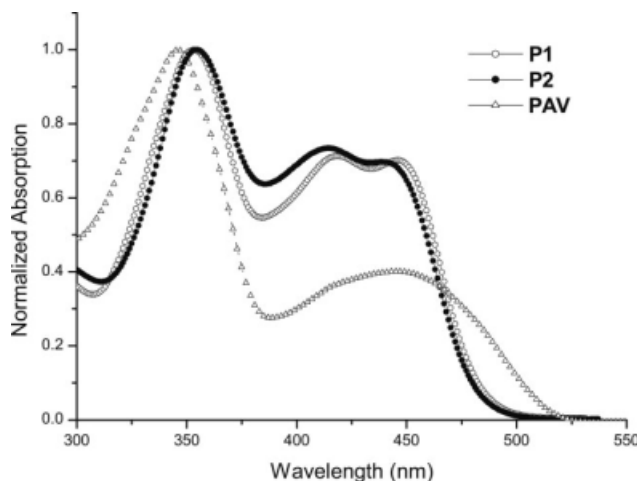


FIGURE 1 UV-Vis absorption spectra of **P1**, **P2**, and **PAV** in toluene solution. Concentration = 1.0×10^{-4} mol L $^{-1}$ in repeating unit.

spectra (λ_{fl}) and the longest wavelength absorption bands (λ_{abs}) of **P1** (λ_{fl} = 491 nm, λ_{abs} \approx 433 nm) and **P2** (λ_{fl} = 483 nm, λ_{abs} \approx 426 nm) are hypsochromatically shifted to some extent compared with that of **PAV** (λ_{fl} = 496 nm, λ_{abs} \approx 446 nm) (Figs. 1 and 2). This implies that the insertion of 3,6- and 2,7-carbazole into **PAV** backbone has shortened the effective conjugation length of the corresponding polymer. On the other hand, although **P1** and **P2** have the similar shape of absorption spectra and almost same absorption onset, the lower energy absorption bands of **P1** and **P2** are located at the different wavelength regions (Fig. 1), which is consistent with their different PL spectra that **P1** shows less blue-shift PL spectrum than **P2**. The different hypsochromic shift of the absorption and emission spectra for **P1** and **P2** indicates that the optical properties of these conjugated materials are highly dependent on both the nature of the active building blocks and the way in which they are linked. It is well known that, in comparison between 3,6- and 2,7-carbazole, 3,6-carbazole has a stronger electron-donating ability and 2,7-carbazole has a better conjugation-extending ability. To this 2,6-anthracenevinylene-based system, the contribution to the spectral blue-shift from the conjugation-extension of 2,7-carbazole is over that from the strong donor strength of 3,6-carbazole. The PL spectra of **P1**, **P2**, and **PAV** are less resolved and reflect the lack of intrachain ordering that is due to the twist structure between phenyl and anthryl ring and plenty of flexible side chains and the kink-like carbazole segments (especially for 3,6-carbazole).²⁸ **P1** and **P2** emit strong bluish-green fluorescence with the PL quantum yields (Φ_f) of 0.85 and 0.78, respectively, measured relative to quinine (Φ_f = 0.50 in 0.5 M H $_2$ SO $_4$).²⁹ These two Φ_f values are significantly higher than that of **PAV** (Table 1).

Two-Photon Optical Properties of Polymer Solutions

We used two-photon-induced fluorescence measurement technique to investigate the two-photon properties of the three polymers. The femtosecond laser pulses (120 fs) were employed for avoiding possible complications due to the

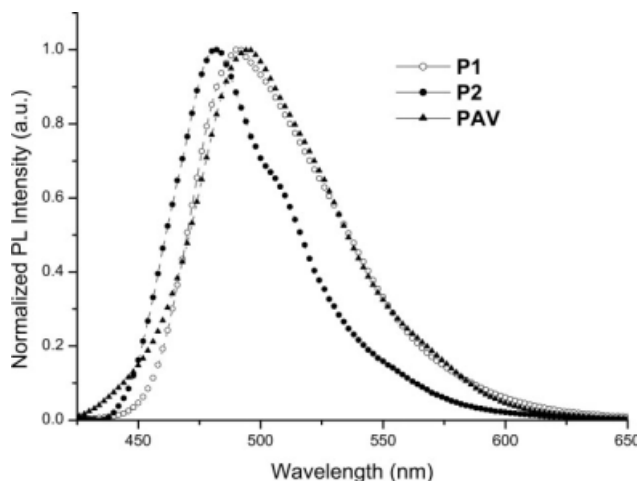


FIGURE 2 One-photon fluorescence spectra of **P1**, **P2**, and **PAV** in toluene. Concentration = 1.0×10^{-4} mol L $^{-1}$ in repeating unit.

excited-state excitation.¹⁵ The polymer concentration is 1.0×10^{-4} mol L $^{-1}$ in repeating unit.

To confirm the occurrence of nonlinear absorption, the two-photon excitation fluorescence of **P1** and **P2** were recorded by changing the input laser powers (20–160 mW) under 800 nm, which falls within the strong linear (one-photon) absorption band of these polymer solutions. These 2,6-anthracenevinylene-based polymers have strong linear absorption around 300–500 nm, but no absorption in the spectral range of 550–1100 nm. If the polymer solutions are irradiated with an 800 nm of laser pulses, there should not be any one-photon absorption induced photoluminescence. However, we have observed the strong fluorescence emission from the polymer solutions under different laser intensities. Figure 3 presents that the output fluorescence intensity of

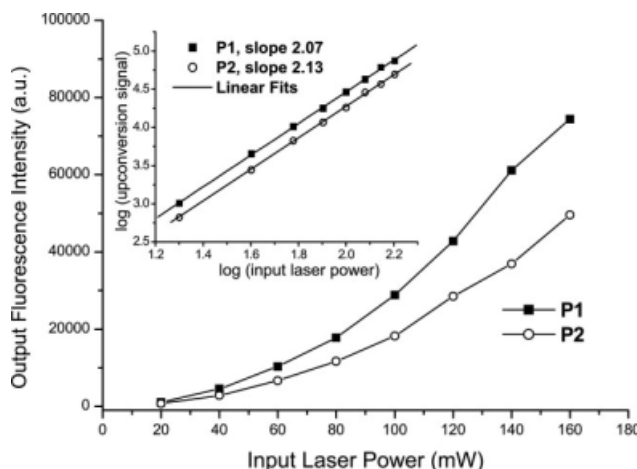


FIGURE 3 The dependence of output fluorescence intensity of polymers **P1** and **P2** in toluene on the input laser power under the excited wavelength of 800 nm. The inset is the linear dependence of logarithmic output fluorescence intensity (up-conversion signal) on logarithmic input laser power. Concentration = 1.0×10^{-4} mol L $^{-1}$ in repeating unit.

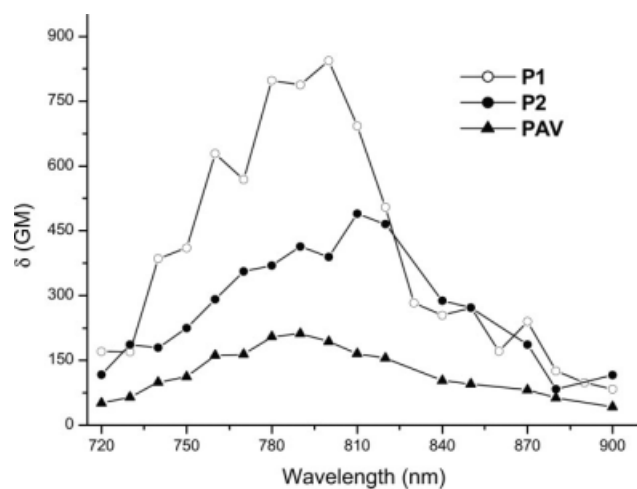


FIGURE 4 Two-photon excitation spectra of **P1**, **P2**, and **PAV** in toluene under the excitation power of 100 mW. Concentration = 1.0×10^{-4} mol L $^{-1}$ in repeating unit.

P1 and **P2** solutions is nonlinearly increased with the input laser power. The plot of logarithmic output fluorescence intensity versus logarithmic input laser power gives a power-law dependence of exponent 2.07–2.13 (the inset of Fig. 3), which is indicative of a two-photon excitation process. As predicted,⁷ there is a good spectral overlap between the one- and two-photon excitation fluorescence for both **P1** and **P2** (Fig. 5, *vide post*), indicating that the fluorescence emission occurs from the same excited states, regardless of the mode of excitation.

The TPA cross-sections (δ) are determined under 100 mW of input laser power (which falls within the power range of two-photon excitation) as a function of excitation wavelength (700–900 nm). The two-photon excitation spectra for **P1**, **P2**, and **PAV** were depicted in Figure 4. The relevant spectroscopic parameters were summarized in Table 1. It can be seen that all polymers exhibited broad TPA bands with the maximal TPA cross-sections (δ_{max}) around 800 nm. The maximal TPA cross-sections (δ_{max}) of **P1**, **P2**, and **PAV** were 840, 490, and 210 GM per repeating unit, respectively. **PAV** shows the smallest TPA cross-sections among these three polymers although the degree of conjugation along polymer backbone for **PAV** is the best. This can be ascribed to the absent donor substituent across the 2,6-anthracenevinylene unit. Comparing between 3,6- and 2,7-linkages of carbazole, 3,6-carbazole is a stronger electron-donating moiety and a weaker conjugation-extending block, but **P1** exhibits obviously larger δ_{max} value than **P2**, which indicates that, at least in this system, the incorporation of strong electron-donating moieties into the polymer backbone to form D- π -D motif is more effective in enhancing TPA cross-sections than the extension of conjugation length. Nevertheless, the δ values of **P1** and **P2** are fairly large and obviously higher than that of the linear and hyperbranched conjugated polymers reported in literatures in terms of femtosecond laser pulses,^{11–17} implying that polymers with large TPA cross-sections can be obtained by employing effective TPA chromophores as the building blocks

(repeating units). It is also interesting to note that **PAV** itself shows appreciable TPA cross-section (210 GM), which is large among poly(arylenevinylene)s reported in literatures in

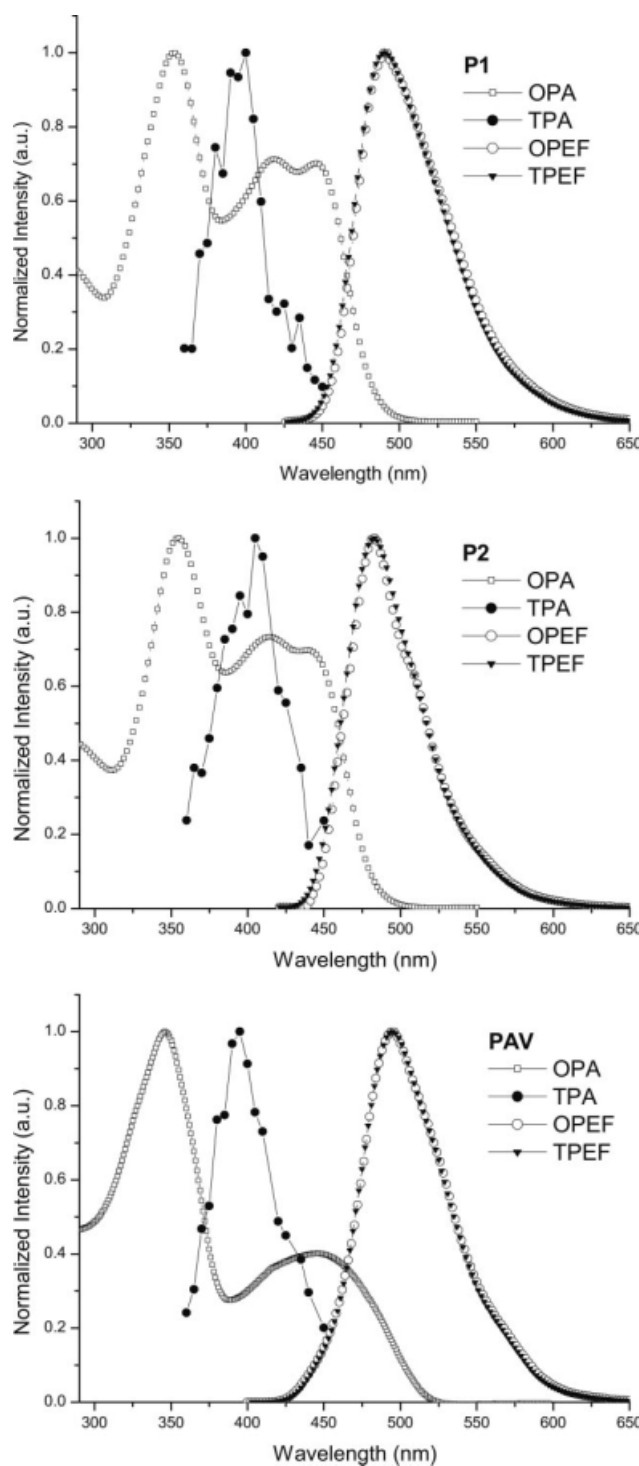


FIGURE 5 Normalized one-photon absorption (OPA) and fluorescence (OPEF), two-photon excitation (TPA) and fluorescence (TPEF) spectra of **P1**, **P2**, and **PAV** in toluene. The two-photon excitation spectra are plotted against $\lambda_{\text{TPA}}/2$ (twice the photon energy).

terms of femtosecond pulses.¹⁵ This might be due to that the large and planar π -center is favor of the increase of TPA cross-sections.⁷ A reasonable comparison among poly(arylenevinylene)s still requires investigation since the measurement of TPA cross-sections is complicated and is interfered with many factors.

The normalized one-photon absorption, fluorescence, and the two-photon fluorescence and excitation spectra for these polymer solutions were depicted in Figure 5. The two-photon allowed state ($\lambda_{\text{TPA}}/2$, twice the photon energy) of **PAV**, **P1**, and **P2** were all located at shorter wavelengths than the longest wavelength absorption bands (the lowest energy absorption maxima). This is consistent with the prediction that the two-photon allowed states for quadrupoles are at a higher energy than the Franck-Condon states (one-photon allowed states).³⁰

CONCLUSIONS

We have synthesized two novel donor-containing 2,6-anthracenevinylene-based copolymers by the Wittig-Horner coupling between 9,10-bis(3,4-bis(2-ethylhexyloxy)-phenyl)-2,6-bis(diethylphosphorylmethyl)anthracene and *N*-octyl-3,6-diformyl-carbazole (**P1**) and *N*-octyl-2,7-diformylcarbazole (**P2**), and their TPA cross-sections (δ_{TPA}) are measured by the two-photon induced fluorescence method using femtosecond pulses. **P1** and **P2** have high-molecular weights ($M_n = 1.6\text{--}1.8 \times 10^4$) and high-fluorescence quantum yields ($\Phi_f = 0.85\text{--}0.78$). They exhibit strong TPA properties and the maximal δ_{TPA} of **P1** and **P2** are 840 GM and 490 GM per repeating unit, respectively. These δ_{TPA} values are obviously higher than that (210 GM) of their reference polymer, **PAV**, indicating that the incorporation of strong electron-donating moieties into the polymer backbone to form D- π -D repeating unit is more effective in enhancing δ_{TPA} than the extension of conjugation length. Polymers with large δ_{TPA} can be obtained by employing effective TPA chromophores as the repeating units.

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