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Conjugated Polymers with Pyrrole as the Conjugated Bridge: Synthesis, Characterization, and Two-Photon Absorption Properties

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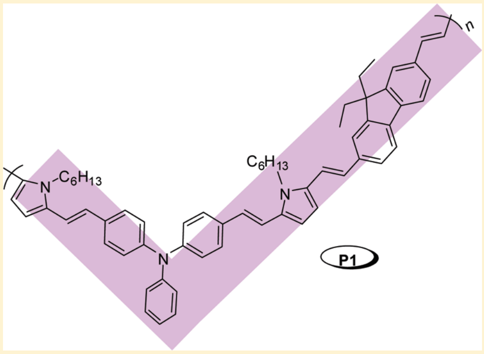
S *Supporting Information*

ABSTRACT: The synthesis, one- and two-photon absorption (2PA) and emission properties of two novel pyrrole-based conjugated polymers (**P1** and **P2**) are reported. They emitted strong yellow-green and orange fluorescence with fluorescent quantum yields (Φ) of 46 and 33%, respectively. Their maximal 2PA cross sections (δ) measured by the two-photon-induced fluorescence method using femtosecond laser pulses in THF were 2392 and 1938 GM per repeating unit, respectively, indicating that the 2PA chromophores consisting of the triphenylamine with nonplanar structure as the donor and electron-rich pyrrole as the conjugated bridge could be the effective repeating units to enhance the δ values.



INTRODUCTION

Conjugated polymers, an important class of multiphoton absorbing materials, are known to provide the advantage of a collective optical response and have attracted increasing attention due to their versatile applications in two-photon cellular imaging, optical power limiting, multiphoton pumped lasing, three-dimensional optical storage, and photodynamic therapy.[1−3] Generally, in the field of two-photon absorption materials, by extending the conjugation length (effective π-delocalization), conjugated polymers with large two-photon absorption (2PA) cross sections can be obtained as a result of their extended intramolecular charge transfer. However, their planar structures have usually caused aggregations and possible interchain quenching; thus, they often have exhibited decreased fluorescence quantum yields, which has limited their applications in some fields that require strong two-photon excited fluorescence (TPEF), such as up-converted lasing and bioimaging. Therefore, there is a need to develop novel 2PA materials, which may circumvent this trade-off.

As an electron-rich, propeller-shaped molecule with C_3 symmetry and good hole transporting ability, coupled with its bulky volume for the prevention of possible aggregation, triphenylamine is often utilized to construct 2PA materials.[4] Interestingly, in comparison with many studies of efficient fluorescent triphenylamine-based branched polymers with high 2PA cross sections, the linear ones bearing triphenylamine as the core have seldom been reported, although they could be synthesized much easier than the branched ones, possibly due to their nonplanar structure, which does not extend the conjugated system as well as the planar ones. To make up this weakness, some electron-excessive heteroaromatic rings, such as furan, thoiphene, and pyrrole, could be used as the conjugation bridge instead of the benzene one to enhance the intramolecular charge transfer.

We are interested in the design and preparation of new pyrrole-based functional materials, since in comparison with the most-used thiophene ring, pyrrole possesses a more abundant electron density, directly leading to more effective charge transfers as a linker between the donors and the acceptors. Our recent work partially proved this point: the pyrrole-containing second-order nonlinear optical (NLO) chromophores showed enhanced NLO effects (up to 3.3 times) and much more blue-shifted maximum absorption (up to 36 nm) than their analogues with furan or thiophene as a conjugated bridge.[5] When pyrrole moieties were introduced into the dye sensitizers as a π-bridge, a high conversion efficiency of 7.21% was achieved for solar-cell devices based on them, which was 91% of the standard cell from N719 under the same test conditions.[6a,b] In addition, some exciting results were reported by the Marder group on pyrrole-based 2PA materials.[7] However, conjugated polymers based on a pyrrole moiety as the 2PA materials are still very scarce.

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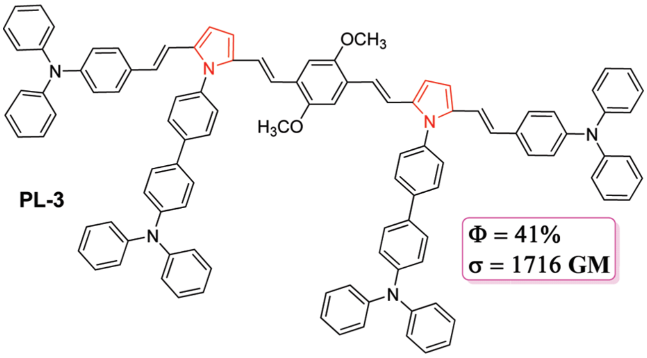
Recently, we designed a series of new pyrrole-based chromophores with the D-π-D structure, which exhibited two-photon absorption activity in the range of 730−900 nm with a large two-photon absorption cross section (~1000−1700 GM).[6c] For example, as shown in Chart 1, **PL-3** demonstrated the two-photon absorption cross section of 1716 GM, with its quantum yield as good as 0.41. Prompted by these results, also considering the above-mentioned points, we further designed and synthesized some pyrrole-containing conjugated polymers with different conjugated linkers for 2PA interest (**P1** and **P2**, Scheme 1). Because there were many successful reports concerning the cooperative enhancement effect observed in multibranched 2PA molecules, we constructed the polymers on the basis of disubstitued triphenylamine moieties. The prepared polymers, **P1** and **P2**, exhibited good solubility in common organic solvents and emitted strong one- and two-photon excitation fluorescence. Their maximal 2PA cross sections, measured by the two-photon-induced fluorescence method using femtosecend laser pulses in THF, were 2392 and 1938 GM, respectively.

■ EXPERIMENTAL SECTION

Materials. Tetrahydrofuran (THF) was dried over and distilled from a K−Na alloy under an atmosphere of dry argon. *N,N*-Dimethylformamide (DMF) was dried over and distilled from CaH_2. 1,2-Dichloroethane was dried over and distilled from phosphorus pentoxide. Phosphorus oxychloride was freshly distilled before use. Compounds **1**,[8] **2**,[5] **5**, and **6**,[9] were prepared according to the literature. All other reagents were used as received.

Instrumentation. ^1H and ^{13}C NMR spectra were measured on a Varian Mercury300 spectrometer using tetramethylsilane (TMS; δ = 0 ppm) as internal standard. The Fourier transform infrared spectra were recorded on a PerkinElmer-2 spectrometer in the region of 3000−400 cm^{-1}. UV−visible spectra were obtained using a Shimadzu UV-2550 spectrometer. Photoluminescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer. EI-MS spectra were recorded with a Finnigan PRACE mass spectrometer. Elemental analyses were performed by a Carloerba-1106 microelemental analyzer. Thermal analysis was performed on Netzsch STA449C thermal analyzer at a heating rate of 10 °C/min in argon at a flow rate of 50 cm^3/min for thermogravimetric analysis (TGA). The thermometer for measurement of the melting point was uncorrected. A mode-locked Ti:sapphire laser (Mai Tai, Spectra-Physics Inc., U.S.A.) was used as the excitation source. The average output power, pulse width, and repetition rate were 0.5 W, 100 fs, and 80 MHz, respectively. After passing through a Pockel cell (350−80 LA BK, Conoptics Inc., U.S.A.) that was used to control the power of the laser, the laser was focused on the cell (polished on all sides) by a focusing lens (f = 6 cm). The emission light was collected by an objective lens (Olympus, Japan) and then was focused by another objective lens on a fiber spectrometer (HR2000, Ocean Optics Inc., U.S.A.), which was used to record the fluorescent spectra. Fluorescein in water was chosen as the reference standard.

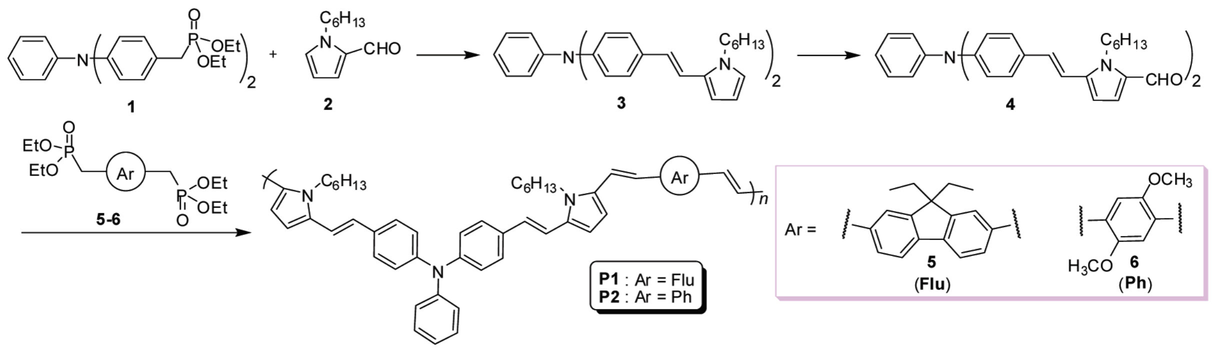
Chart 1



Synthesis of Compound 3. Compound **1** (1.32 g, 2.42 mmol) was suspended in 20 mL of anhydrous tetrahydrofuran under an atmosphere of dry argon. *t*-BuOK (1.14 g, 11.16 mmol) was added directly as a solid, and the resultant mixture was stirred at room temperature for 10 min. After the addition of the solution of compound **2** (0.91 g, 5.08 mmol) in anhydrous tetrahydrofuran (10 mL) dropwise, the reaction mixture was stirred at room temperature overnight, then poured into 100 mL of water. The organic product was extracted with chloroform and dried over anhydrous Na_2SO_4. After removing the solvent, the crude product was purified through a silica gel chromatography column by using petroleum/ethyl acetate (10/1) as eluent to afford yellow oil **3** (1.03 g, 71.5%). ^1H NMR ($CDCl_3$) δ (ppm): 7.35−7.26 (m, 5H, ArH and −CH═CH−), 7.14−7.00 (m, 10 H, ArH and −CH═CH−), 6.84 (s, br, 6H, ArH), 6.16 (s, br, 2H, ArH), 3.95 (t, 4H, J = 6.6 Hz, −N−CH_2−), 1.75 (s, br, 4H, −CH_2−), 1.31 (s, br, 12H, −CH_2−), 0.88 (s, br, 6H, −CH_3).

Synthesis of Compound 4. DMF (0.38 g, 5.20 mmol) was added to freshly distilled $POCl_3$ (0.66 g, 4.32 mmol) under an atmosphere of dry argon at 0 °C, and the resultant solution was stirred until its complete conversion into a glassy solid. After the addition of 1,2-dichloroethane (10 mL), the resultant colorless solution was added dropwise at 0 °C to a yellow solution of

Scheme 1



compound **3** (1.03 g, 1.73 mmol) in 1,2-dichloroethane (10 mL). The mixture was stirred at room temperature overnight, then poured into an aqueous solution of sodium acetate (1 M, 100 mL) and stirred for another 2 h. The mixture was extracted with chloroform several times, and the organic fractions were collected and dried over Na_2SO_4. After removing the solvent under vacuum, the crude product was purified through a silica gel chromatography column by using chloroform as eluent to afford yellow solid **4** (0.78 g, 69.2%). M_p = 144−145 °C ^{1}H NMR ($CDCl_3$) δ (ppm): 9.45 (s, 2H, −CHO), 7.39 (d, 4H, J = 8.1 Hz, ArH), 7.34−7.26 (m, 3H, ArH and −CH═CH−), 7.16−7.07 (m, 8H, ArH), 6.92 (d, 2H, J = 4.5 Hz, ArH), 6.86 (d, 2H, J = 16.2 Hz, −CH═CH−), 6.55 (d, 2H, J = 3.6 Hz, ArH), 4.45 (t, 4H, J = 8.1 Hz, −N−CH_2−), 1.75 (s, br, 8H, −CH_2−), 1.31 (s, br, 12H, −CH_2−), 0.86 (s, br, 6H, −CH_3). ^{13}C NMR ($CDCl_3$) δ (ppm): 178.7, 147.7, 147.1, 141.5, 132.5, 132.2, 131.3, 129.8, 127.9, 125.5, 124.3, 124.0, 113.8, 107.9, 45.3, 31.7, 31.6, 26.5, 22.8, 14.3. IR (thin film), υ (cm^{-1}): 1652 (−CHO). MS (EI), m/z [M$^+$] 651.17, calcd 651.38. Anal. Calcd for $C_{44}H_{49}N_3O_2$: C, 81.07; H, 7.58; N, 6.45;. Found: C, 81.07; H, 7.26; N, 6.18.

General Procedure for Preparation of Polymers P1 and P2. To ice-cold solutions of compound **4** (1 equiv) and compounds **5**−**6** (1 equiv) in dry THF was added t-BuOK (2 equiv) (1.0 M in THF solution) dropwise under an atmosphere of dry argon. The reaction mixture was stirred overnight at room temperature. The THF was evaporated, and methanol was added to precipitate the product. The polymer was further purified by reprecipitation with acetone/MeOH.

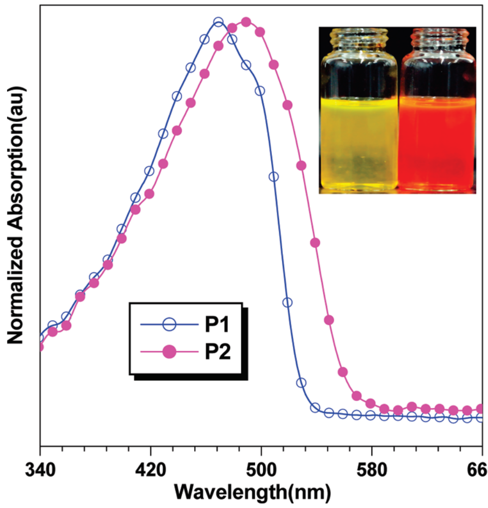


Figure 1. Normalized UV−vis spectra of the polymers in THF. Concentration: 1.0 × 10^{-6} M in repeating unit. Inset: photographs of the polymers in THF, **P1** (left) and **P2** (right).

P1: compound **4** (130 mg, 0.20 mmol), compound **5** (104 mg, 0.20 mmol). Orange solid (150 mg, 64.1%). M_w = 2.10 × 10^4, M_w/M_n = 1.14 (GPC, polystyrene calibration). IR (thin film), υ (cm^{-1}): 1655 (terminal CHO). ^{1}H NMR ($CDCl_3$) δ (ppm): 9.5 (trace terminal −CHO), 7.7 (ArH), 7.5 (ArH), 7.4 (ArH), 7.3−7.0 (ArH and −CH═CH−), 6.6 (ArH), 4.5 (−N−CH_2−), 2.1 (−CH_2−), 1.8 (−CH_2−), 1.6 (−CH_2−), 1.4 (−CH_2−), 0.9 (−CH_3). ^{13}C NMR ($CDCl_3$) δ (ppm): 150.9, 148.0, 147.5, 146.7, 141.6, 140.8, 137.0, 133.4, 133.3, 132.7, 132.1, 129.7, 127.8, 127.0, 125.9, 125.7, 125.1, 125.0, 124.8, 124.3, 123.5, 120.7, 120.0, 116.3, 116.0, 115.7, 113.4, 107.8, 62.5, 56.2, 45.3, 43.5, 33.1, 31.7, 26.7, 26.5, 22.8, 16.7, 14.3.

P2: compound **4** (130 mg, 0.20 mmol), compound **6** (87.4 mg, 0.20 mmol). Red solid (120 mg, 55.2%). M_w = 2.28 × 10^4, M_w/M_n = 1.12 (GPC, polystyrene calibration). IR (thin film), υ (cm^{-1}): 1652 (terminal −CHO). ^{1}H NMR ($CDCl_3$) δ (ppm): 9.5 (trace terminal −CHO), 7.3 (ArH), 7.2−7.0 (ArH and −CH═CH−), 6.9 (ArH), 6.6 (ArH), 4.5 (−N−CH_2−), 4.1 (−O−CH_2−), 1.8 (−CH_2−), 1.3 (−CH_2−), 0.9 (−CH_3). ^{13}C NMR ($CDCl_3$) δ (ppm): 151.9, 148.3, 147.8, 147.5, 146.9, 146.5, 141.9, 134.1, 133.6, 133.0, 132.4, 131.0, 130.0, 128.5, 128.0, 127.3, 126.9, 126.1, 125.9, 125.4, 125.1, 124.6, 124.1, 123.7, 121.5, 118.4, 118.0, 116.0, 115.1, 113.7, 109.8, 109.4, 108.3, 108.1, 62.5, 56.8, 56.7, 45.5, 43.8, 31.9, 30.2, 27.0, 26.8, 23.1, 16.9, 14.5.

RESULTS AND DISCUSSION

Synthesis and Characterization. The synthetic route to the polymers is given in Scheme 1. Compound **1** was synthesized according to the previous literature in three-step sequences: a Vismeier reaction of triphenyl amine yielded the aldehyde, then the deoxidization of the aldehyde group with $NaBH_4$, followed by the reaction with triethyl phosphate.[8] The intermediate **3** was obtained by means of a double Wittig−Horner−Emmons olefination of compounds **1** and **2** in the presence of t-BuOK in THF with satisfactory yields (71.5%). The conversion of compound **3** to the corresponding bisaldehydes **4** was achieved by the Vilsmeier reaction, then the preparation of the polymers **P1** and **P2** followed by Wittig−Horner−Emmons olefination using the required bisphosphonates with the yields of 64.1% and 55.2% for fluorenylene and 1,4-dimethoxyphenylene moieties, respectively. By utilizing this approach, different aryl moieties could be conveniently introduced into this system through C═C bonds.

The polymers **P1** and **P2** were soluble in common organic solvents, such as THF, chloroform, DMF, and DMSO. The

Table 1. Some Characterization Data of Polymers

polymers	yield (%)	M_w (× 10^4)[a]	M_w/M_n[a]	λ_{max}^{abs} (nm)[b]	λ_{max}^{abs} (nm)[c]	λ_{max}^{em} (nm)[d]	λ_{max}^{em} (nm)[e]	λ_{max}^{tp} ^{tp} (nm)[f]	Φ (%)[g]	δ (GM)[h]	T_d (°C)[i]
P1	64.1	2.10	1.14	469	469	533	555	760	46	2392	369
P2	55.2	2.28	1.12	489	489	569	597	760	33	1938	362

[a] Determined by GPC in DMF on the basis of a polystyrene calibration. [b] 1.0 × 10^{-6} M per repeating unit in THF, wavelength of maximum absorbance. [c] UV−vis spectra of polymers in thin film, wavelength of maximum absorbance. [d] 1.0 × 10^{-6} M per repeating unit in THF, wavelength of maximum intensity. [e] PL spectra of polymers in thin film, wavelength of maximum intensity. [f] 2.0 × 10^{-5} M per repeating unit in THF, wavelength of maximum 2PA cross sections. [g] Quantum yields in THF solution using fluorescein in water (Φ_F = 90%, pH = 11) as a standard. [h] 2PA cross sections, 1 GM (Göppert−Mayer) = 10^{-50} cm^4 s photon^{-1}, the experimental uncertainty on δ_{max} is on the order of 10−15%. [i] The 5% weight loss temperature of polymers detected by the TGA analyses under argon at a heating rate of 10 °C/min.

monomer and polymers were characterized by FT-IR and ^{1}H and ^{13}C NMR. The strong peak of the aldehyde group of the momomer was observed at about 1652 cm^{-1} in the FT-IR spectra, and in those of the polymers, the peak around 1652 cm^{-1} could still be observed due to the presence of the terminal aldehyde group. This fact was further confirmed by their ^{1}H NMR spectra. As measured by TGA, the polymers were found to exhibit very good thermal stability, with the initial decomposition temperature above 360 °C under the atmosphere of argon, where over 95% of their mass was retained (Figure 1 and Table 1).

One-Photon Physical Properties. Absorption and emission spectra of polymers were measured in THF solution at a concentration of 1.0 × 10^{-6} M per repeating unit (Figure 1 and Figure 2), with the corresponding photophysical data summarized in Table 1. UV−vis spectra of polymers **P1** and **P2** showed broad absorption maxima at 469 and 489 nm, respectively, which should be assigned to the $\pi-\pi^*$ transition of the conjugated system, indicating that 1,4-dimethoxyphenylene moieties as the conjugated bridge could contribute more to the effective charge transfer from the donor groups to the π-bridge than the fluorenylene group. Although the fluorenylene group possessed the larger planar structure than the phenylene moieties, the two methyloxy groups substituted on the phenyl ring would increase the electron density of the phenylene moieties, thus benefitting the intramolecular charge transfer. As shown in Figure 1, the color of the polymers in THF solution changed from yellow to orange for **P1** and **P2**, suggesting that the different aryl moieties incorporated into the conjugated system through the C═C bond could tune the electron properties of the corresponding polymers expediently.

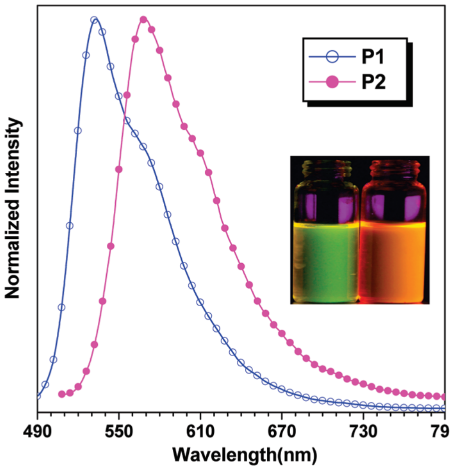


Figure 2. Normalized fluorescence spectra of the polymers in THF. Concentration: 1.0 × 10^{-6} M in repeating unit. Inset: fluorescence photographs of the polymers in THF under UV illumination, **P1** (left) and **P2** (right).

With the same trend as observed in their UV−visible absorption, **P2** exhibited red-shifted emission spectra compared with that of **P1**. The same red-shifted absorption and emission spectra from **P1** to **P2** indicated that the optical properties of these conjugated materials were highly dependent on the nature of the active building blocks. **P1** and **P2** emitted strong yellow-green and orange fluorescence with the PL quantum yields (Φ) of 46 and 33%, respectively, by using fluorescein in water (Φ_F = 90%, pH = 11) as the reference. The relatively higher Φ values might be due to the twist structure of the triphenylamine group and the electron-rich property of the pyrrole ring.

To explore the optical properties of these polymers in the solid state, their absorption and PL properties were investigated (Figure 3), and the corresponding data are summarized in Table 1. The absorption spectra of dilute solutions and solid film were similar, and the maximum absorption wavelengths were the same, which partially disclosed that there was little ground-state aggregation in the solid state. Subsequently, to confirm the result, several experiments were conducted. First, the absorption spectra of polymers in different concentrations were tested (Figures S5 and S6 of the Supporting Information). The shape of the absorption spectra changed only a little accompanied by the growth of the concentrations, and the maximum absorption wavelengths were the same as that in the solid film, indicating that the ground-state interactions between polymer chains were similar from the dilute solutions, to concentrated solutions, then to solid films. Second, the excitation spectra of the long wavelength bands in thin films mostly remained unchanged upon the excitation of different emission wavelengths (Figure S7 of the Supporting Information), and the same phenomena were observed in their solutions (Figure S8 of the Supporting Information), further indicating that the aggregate formation was inhibited in the ground state.

To get an insight into the molecular structure and electron distribution of the polymers, the geometries and frontier orbitals

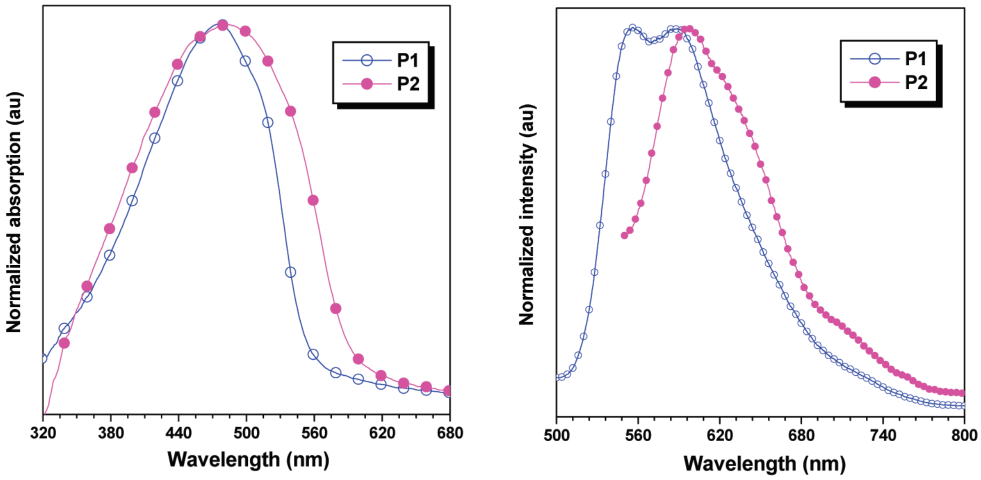


Figure 3. Normalized solid-state absorption spectra (left) and normalized solid-state PL spectra (right) of the polymers.

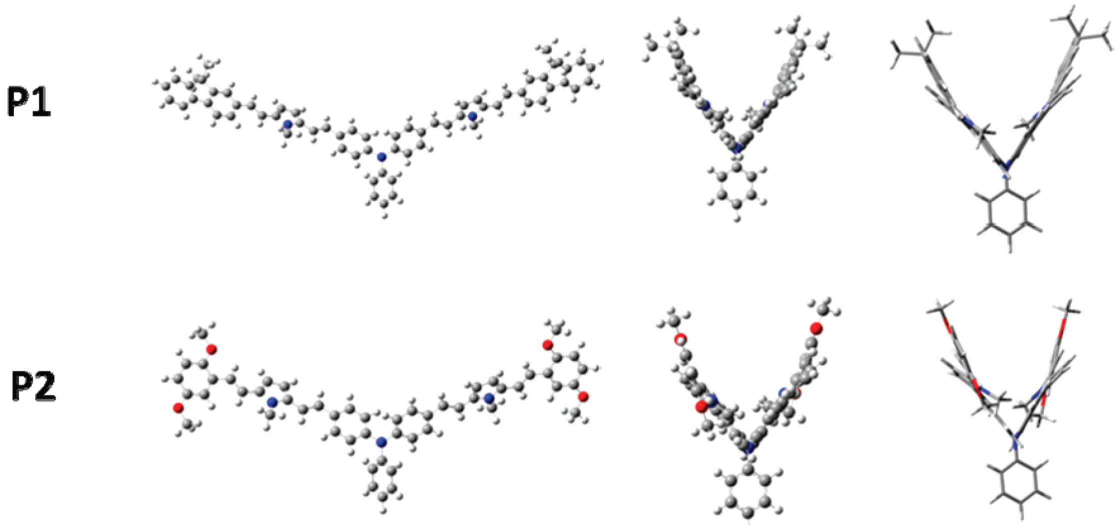


Figure 4. The repeating units of polymers **P1** and **P2** optimized at the B3LYP/6-31+G(D) level.

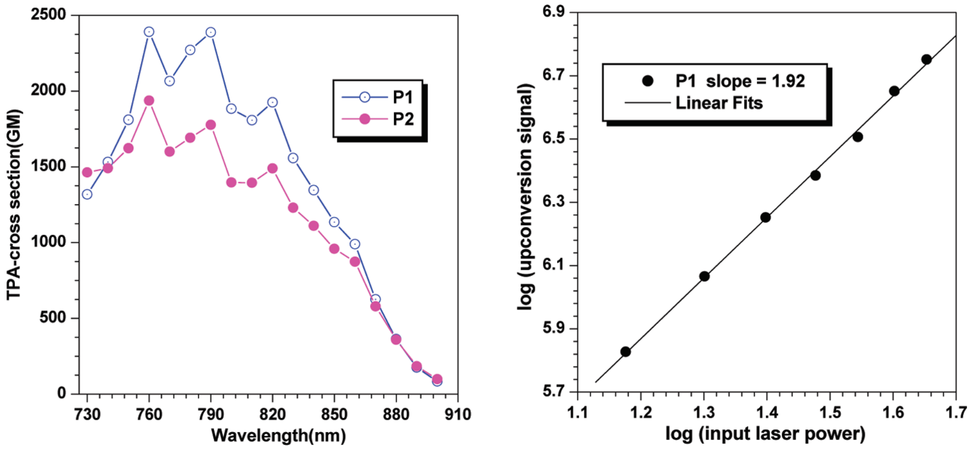


Figure 5. Two-photon absorption cross section (δ) of polymers in THF (left) and the dependence of logarithmic output fluorescence intensity (upconversion signal) on logarithmic input laser power under the excited wavelength of 800 nm (right). Concentration: 2.0 × 10^{-5} M in repeating unit.

of the repeating units of polymers **P1** and **P2** have been optimized by using time-dependent DFT (TDDFT) calculations with the Gaussian 03 program (Figure 4 and Figure S4 of the Supporting Information). It was easily seen that the nonplanar structure of triphenylamine as the core led to the twisted configuration of the repeating units, which could inhibit the aggregated formation.

The high fluorescence of polymers in solution was partially quenched in the solid state, with their maximum emissions at 555 and 597 nm, respectively, which were about 22 and 28 nm red-shifted from those in solutions. Considering all the above facts, the long-wavelength emission in the solid state should be ascribed to the formed excimers rather than the possible ground-state aggregations. However, the increase in the effective conjugation length in the solid states could also result in the red-shifted emission spectra.

Two-Photon Absorption Properties. The two-photon cross sections of polymers in THF at a concentration of 2 × 10^{-5} M in repeating unit were measured by the two-photon induced fluorescence technique, using femtosecond laser pulses.[10] The femtosecond laser pulses (100 fs) were employed to avoid possible complications due to the excited-state excitation, and the thermooptical effect could be ignored. To confirm the occurrence of nonlinear absorption, we have investigated the strong fluorescence emission from the polymer solutions under different laser intensities, and the output fluorescence intensity was nonlinearly increased with the input laser power. The plot of logarithmic input laser power gave a power law dependence of exponent 1.92 (Figure 5), which was indicative of a two-photon excitation process. The 2PA spectra of the polymers in THF were presented in Figure 5, with the excitation wavelength in the range of 730−900 nm. The relevant spectroscopic parameters are summarized in Table 1. The δ values were calculated according to the following equation:[11]

$$\delta_{2s} = \frac{F_s}{F_r} \times \frac{\Phi_r n_r c_r}{\Phi_s n_s c_s} \delta_{2r}$$

The subscripts s and r stand for the measured sample and reference molecule, respectively; F is the integrated fluorescence intensity measured at the same power as the excitation beam; Φ is the fluorescence quantum yield; c is the number density of the molecules in the solution. The δ_{2r} term is the 2PA cross section

Table 2. Some Parameters of Polymers for Normalized TPA Cross Sections

	N_{eff} [a]	E_{10} (eV) [b]	E_{20} (eV) [c]	n [d]	$\delta_{\max}$ (GM) [e]	$\delta/\delta_{\max}$ [f]
P1	40.5	2.64	3.26	1.405	2392	0.0032
P2	36.5	2.54	3.26	1.405	1938	0.0023
PL-3	41.6	2.66	3.26	1.405	1716	0.0022

[a] The effective number of electrons in the molecules or the repeating unit of polymers. [b] The transition energy between the one-photon excited state and the ground state, which is given by $E_{10} = 1240/\lambda_{\max}^{\text{em}}$. [c] The transition energy between the two-photon excited state and the ground state, which is given by $E_{20} = 2 \times 1240/\lambda_{\max}^{\text{tp}}$. [d] The refractive index of THF. [e] Two-photon absorption cross sections in repeating unit, 1 GM (Göppert−Mayer) = 10^{-50} cm^4 s photon^{-1}. [f] The normalized two-photon absorption cross sections.

of the reference molecule. Here, fluorescein was chosen as the reference molecule.

It could be easily seen that **P1** and **P2** exhibited broad 2PA bands with the maximum 2PA cross sections (δ) around 760 nm. The maximum 2PA cross sections of polymers **P1** and **P2** were 2392 and 1938 GM per repeating unit, respectively. The large δ value implied that the 2PA chromophores consisting of the triphenylamine and pyrrole could be the effective building blocks (repeating units). **P1** exhibited a little larger δ value than **P2**, indicating that, in this system, the extension of conjugation length was more effective in enhancing 2PA cross-section than the incorporation of electron-donating moieties, which might be due to the strong electron-rich property of the pyrrole ring.

According to Kuzyk's electron rules,[12] the normalized 2PA cross sections were calculated to determine the 2PA cross sections per electron, with the data summarized in Table 2. The trend for the normalized 2PA cross sections was similar to the absolute values. Since **PL-3** has a similar structure with the repeating unit of polymer **P2**, it could be seen that the 2PA cross sections of **P2** in the repeating unit were larger than the single chromophore, suggesting that it was a good approach for the enhancing of the 2PA cross sections to connect the chromophore moieties together to construct the corresponding conjugated polymers.

CONCLUSIONS

In this work, two novel conjugated polymers, **P1** and **P2**, with triphenylamine as the donor and pyrrole and fluorenylene or 1,4-dimethoxyphenylene moieties as the connecting unit, were synthesized by Wittig−Horner−Emmons olefination. They were soluble in common organic solvents and emitted strong one- and two-photon excitation fluorescence in dilute THF solution. The 2PA properties were studied by the two-photon induced fluorescence measurement technique, and the 2PA cross sections of 2392 and 1938 GM were obtained for the polymers **P1** and **P2** per repeating unit, respectively. The results showed that the linear conjugated polymers consisting of triphenylamine and pyrrole would be promising candidates for the further development of novel 2PA materials.

ASSOCIATED CONTENT

S Supporting Information. FT-IR spectra, TGA curves, UV−vis spectra, PL spectra and excitation spectra of polymers, and Frontier orbitals of the repeating units of polymers. This information is available free of charge via the Internet at http://pubs.acs.org.

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