Synthesis and Two-Photon Absorption Properties of Conjugated Polymers with *N*-Arylpyrrole as Conjugated Bridge and Isolation Moieties

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ABSTRACT: Three novel conjugated polymers with *N*-arylpyrrole as the conjugated bridge were designed and synthesized, which emitted strong one- or two-photon excitation fluorescence in dilute tetrahydrofuran (THF) solution with high quantum yields. The maximal two-photon absorption (TPA) crosssections of the polymers, measured by the two-photon-induced fluorescence method using femtosecond laser pulses in THF, were 752, 1114, and 1869 GM, respectively, indicating that the insertion of electron-donating or electron-withdrawing moieties into the polymer backbone could benefit to the increase of the TPA cross-section. Their large TPA cross-sections, coupled with the relatively high emission quantum yields, made these conjugated polymers attractive for practical applications, especially two-photon excited fluorescence. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 2538–2545, 2011

KEYWORDS: conjugated polymers; copolymerization; isolation; NLO; pyrrole; two-photon absorption

INTRODUCTION Conjugated materials with two-photon absorption (TPA) properties have gained great interest for their potential applications in fluorescence imaging of biological samples, optical limiting, photodynamic therapy, three-dimensional optical data storage, and microfabrication.¹⁻¹¹ According to various design strategies, many conjugated materials, including small molecules and polymers, have been successfully prepared.¹²⁻²³ Especially, for small molecules, it is now apparent that the appropriate design strategy involves symmetrically substituted system with a general structure of the type of D– π –D or A– π –A, where A is an acceptor group, D a donating one, and π a conjugating moiety. Generally, the increase of the donor/acceptor strength, the conjugation length, and the planarity of the π center can effectively improve the TPA cross-section (σ) of the corresponding molecule. Thanks to the enthusiastic efforts of scientists, the effect of varying the electronic properties of the terminal groups and π bridge in small molecules have been investigated in detail,²⁴⁻²⁸ giving some useful rules to obtain molecules with high TPA activities. To be applied in some practical applications, small TPA molecules should be incorporated into the host polymer to avoid the possible aggregation at high concentrations. However, their disperse concentration in the host polymer matrix is limited by the phase separation in a large degree. As an alternative approach, the conjugated polymers have attracted more and more interest, which offered enhanced TPA effects.

Actually, in most of the reported conjugated TPA polymers, such as ladder-type poly(*p*-phenylene), poly[1,6-bis(3,6dihexadecyl-N-carbazolyl)-2,4-hexadiyne], polyfluorene, and poly(*p*-phenyleneethynylene), the intramolecular charge transfer was relatively weak, resulting in the relatively lower σ .²⁹⁻³² Thus, TPA chromophores with large σ were used as building blocks or repeating units in the conjugated polymers, to enhance their σ values. However, the aggregation in their concentrated solutions or solid state due to the long conjugation chains and the planar structure of the conjugation polymers, usually quenched their emission, leading to the TPA efficiency/fluorescence tradeoff, which, as a result, limited their applications in some fields that required strong two-photon excited fluorescence (TPEF), such as upconverted lasing and bioimaging. To suppress the aggregation, some hyperbranched polymers and dendrimers containing TPA-active units have been synthesized.³³⁻³⁶ Their threedimensional architectures gave them advantages for TPA.

Recently, some exciting results have been obtained from pyrrole-containing materials in several different research fields, including photochemistry, second-order nonlinear optical and TPA materials.³⁷⁻⁴⁷ Also, our previous research demonstrated that *N*-arylpyrrole as the building block could efficiently improve the stability of the resultant chromophores compared to that of the *N*-alkylpyrrole-based analogs.^{48–50} More importantly, the introduced central aryls could hinder

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CHART 1 The structure of dye **LI-1** with *N*-arylpyrrole as the conjugated bridge. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the π - π stacking and aggregation process (i.e., the red part in Chart 1). For example, when *N*-arylpyrrole moieties were introduced into the dye sensitizers (LI-1, Chart 1) as π bridge, a high conversion efficiency of 7.21%, 91% of the standard cell from N719 tested under similar measuring conditions was obtained from the corresponding solar-cell device. Additionally, pyrrole, as an electron-rich heterocyclic ring, could act as the auxiliary donor to enhance the intramolecular charge transfer from the terminal donor groups to the π bridge. Thus, *N*-arylpyrrole might be a novel conjugation moiety for optimizing TPA efficiency/fluorescence tradeoff, as different aryl groups could be conveniently introduced through the carbon-nitrogen bond.

On the other hand, in 2006, for the first time, we attempted to link two pieces of donor- π -acceptor blocks together through an isolation group to yield a new type of chromophore, which we termed as "H"-type chromophores (Chart 2).⁵¹ After embedded into the polymeric system, the resultant polyurethanes containing this "H"-type chromophore (PS2, Chart 2) exhibited enhanced second-order nonlinear optical effects in comparison with their linear analogs (PS1, Chart 2), realizing the effect of "one plus one greater than two," partially due to the presence of the isolation group, which weakened the aggregation of the donor- π -acceptor blocks. Our other examples and some cases reported by

other scientists also confirmed this effect.^{52–54} Thus, we wondered, how about the results if TPA chromophore moieties were bonded together through an isolation group?

Therefore, all the above points prompted us to prepare some novel conjugated polymers, in which the N-arylpyrrole-based TPA chromophore moieties were linked together through an isolation group, with triphenylamine group acting as threedimensional bulky moiety similar to dendritic ones, generally present in dendrimers and hyperbranched polymers, to suppress the aggregations as possible. Just as shown in Chart 3, we have successfully obtained these new kinds of polymers, P1-P3. Furthermore, the optical properties of the polymers could be subtly tuned by introducing various substituted conjugated aromatic rings bearing the donating and/or withdrawing abilities (the Ar group in Chart 3). All the polymers (P1-P3) exhibited good solubility (in common organic solvents), high thermal stability, satisfied quantum yields, and good TPA properties, with the highest σ value achieved as large as 1869 GM for P3 at 760 nm.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF) was dried over and distilled from a K-Na alloy under an atmosphere of dry nitrogen. Compounds **3–5** were prepared according to the literature.^{55–57} All other reagents were used as received.

Instrumentation

¹H and ¹³C NMR spectra were measured on a Varian Mercury300 spectrometer using tetramethylsilane ($\delta = 0$ ppm) as internal standard. The Fourier transform infrared spectra were recorded on a Perkin-Elmer-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. Molecular weights (M_w and M_n) and polydispersity indices (M_w/M_n) of the polymers were estimated by a Waters 1515 gel permeation chromatography (GPC) system equipped with interferometric refractometer detector, using a set of monodisperse polystyrenes as calibration standards and THF as the eluent at a flow rate of 1.0 mL/min. Elemental analyses were performed by a



CHART 2 The structures of polymers PS1 and PS2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



CHART 3 Schematic representation of monomers and polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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 cm³/ min for thermogravimetric analysis. The thermometer for the measurement of the melting point was uncorrected. A modelocked Ti:sapphire laser (Mai Tai, Spectra-Physics, Santa Clara, CA) 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, Danbury, CT) 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 = 6cm). 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), which was used to record the fluorescent spectra. Fluorescein in water was chosen as the reference standard.

Synthesis of Compound 2

A mixture of compound **1** (1.50 g, 2.89 mmol), 2,2'-(9,9dihexyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (0.69 g, 1.38 mmol), sodium carbonate (3.06 g, 28.9 mmol), and a catalytic amount of tetrakis(triphenylphosphine) palladium (Pd(PPh₃)₄) was carefully degassed and charged with nitrogen. Subsequently, THF (40 mL) and deoxidized water (20 mL) were added by syringe. The reaction mixture was stirred at 80 °C for 48 h. After cooled to room temperature, the organic layer was separated, dried over sodium sulfate, and evaporated to dryness. The crude product was purified through a silica gel chromatography column by using petroleum/ethyl acetate (6/1) as an eluent to afford a yellow solid **2** (1.65 g, 47.1%). mp: 144–145 °C.

¹H NMR (CDCl₃) δ (ppm): 10.03 (s, 1H, —CHO), 9.44 (s, 1H, —CHO), 7.81 (s, br, 8H, ArH), 7.68–7.56 (m, 4H, ArH), 7.48 (d, 2H, J = 7.2 Hz, ArH), 7.43 (d, 2H, J = 7.5 Hz, ArH), 7.26– 7.20 (m, 8H, ArH), 7.11–6.74 (m, 24H, ArH and —CH=CH—), 6.53 (d, 2H, J = 16.8 Hz, —CH=CH—), 2.07 (s, br, 4H, —CH₂—), 1.07 (s, br, 16H, —CH₂—), 0.74 (s, br, 6H, —CH₃). ¹³C NMR (CDCl₃) δ (ppm): 186.4, 178.4, 152.2, 148.5, 148.3, 147.5, 142.4, 142.1, 141.8, 140.7, 140.0, 139.2, 138.1, 136.1, 134.0, 132.2, 130.4, 129.9, 129.6, 128.9, 128.4, 128.1, 127.8, 126.6, 125.8, 125.1, 124.8, 123.7, 123.1, 122.5, 121.8, 121.6, 120.6, 120.3, 115.2, 114.2, 113.8, 110.1, 109.0, 108.1, 55.7, 40.8, 31.8, 30.0, 24.1, 22.9, 14.3. MS (EI), m/z [M+1]⁺: 1211.3, calcd, 1210.6. Anal. Calcd for: C₈₇H₇₈N₄O₂: C, 86.25; H, 6.49; N, 4.62; Found: C, 86.68; H, 6.42; N, 4.56.

General Procedure for Preparation of Polymers P1-3

t-BuOK (2 equiv.; 1.0 M in THF solution) was added dropwise to ice-cold solutions of compound 2 (1 equiv.) and one of compounds 3-5 (1 equiv.) in dry THF. The reaction mixture was stirred overnight at room temperature. THF was evaporated, and methanol was added to precipitate the product. The polymers were further purified by reprecipitation with acetone/MeOH.

P1

Compound **2** (121.2 mg, 0.10 mmol), compound **3** (52.3 mg, 0.10 mmol). Orange solid (120 mg, 67.0%). $M_{\rm w} = 0.30 \times 10^4$, $M_{\rm w}/M_{\rm n} = 1.52$ (GPC, polystyrene calibration). IR (thin film), ν (cm⁻¹): 1663 (terminal-CHO).

¹H NMR (CDCl₃) δ (ppm): 10.0 and 9.45 (trace terminal-CHO), 7.8 (ArH), 7.6–7.5 (ArH), 7.2 (ArH), 7.0 (ArH and –CH=CH–), 6.8–6.5(ArH and –CH=CH–), 2.1(–CH₂–), 1.6 (–CH₂–), 1.1(–CH₂–), 0.7(–CH₃). ¹³C NMR (CDCl₃) δ (ppm): 147.4, 130.3, 130.0, 129.6, 128.9, 128.4, 128.0, 127.8, 127.4, 126.5, 125.0, 124.7, 124.5, 124.1, 123.9, 123.7, 123.0, 121.7, 120.6, 55.7, 40.7, 31.7, 29.9, 24.1, 22.8, 14.3.

P2

Compound **2** (181.7 mg, 0.15 mmol), compound **4** (65.8 mg, 0.15 mmol). Red solid (150 mg, 61.0%). $M_{\rm w} = 0.77 \times 10^4$, $M_{\rm w}/M_{\rm n} = 1.57$ (GPC, polystyrene calibration). IR (thin film), v (cm⁻¹): 1665 (terminal-CHO).

¹H NMR (CDCl₃) δ (ppm): 10.0 (trace terminal-CHO), 7.8 (ArH), 7.6 (ArH), 7.4 (ArH), 7.2 (ArH), 7.0 (ArH and -CH=CH-), 6.8–6.5(ArH and -CH=CH-), 3.9–3.7 ($-O-CH_3$), 2.1($-CH_2-$), 1.6 ($-CH_2-$), 1.1($-CH_2-$), 0.7($-CH_3$). ¹³C NMR (CDCl₃) δ (ppm): 152.2, 147.8, 147.5, 146.9, 140.6, 139.3, 136.8, 132.3, 129.5, 128.0, 127.2, 127.0, 126.5, 125.1, 124.7, 124.6, 124.0, 123.3, 123.1, 121.6, 120.6, 116.6, 107.9, 56.6, 55.7, 40.7, 31.7, 29.9, 24.1, 22.8, 14.3.

P3

Compound **2** (181.7 mg, 0.15 mmol), compound **5** (64.3 mg, 0.15 mmol). Dark red solid (180 mg, 73.2 %). $M_{\rm w} = 2.47 \times 10^4$, $M_{\rm w}/M_{\rm n} = 1.88$ (GPC, polystyrene calibration). IR (thin film), v (cm⁻¹): 1666 (terminal-CHO).

¹H NMR (CDCl₃) δ (ppm): 10.0 (trace terminal-CHO), 7.9–7.6 (ArH), 7.2 (ArH), 7.0–6.5 (ArH and -CH=CH-), 2.1($-CH_2-$), 1.6 ($-CH_2-$), 1.1($-CH_2-$), 0.7($-CH_3$). ¹³C NMR (CDCl₃) δ (ppm): 152.2, 147.7, 140.8, 139.0, 133.3, 132.7, 129.6, 128.3, 128.0, 127.3, 126.8, 126.3, 124.9, 124.7,



SCHEME 1 The synthetic route to polymers P1-3.

123.5, 121.7, 120.6, 115.7, 55.7, 40.7, 31.7, 30.0, 24.1, 22.8, 14.3.

RESULTS AND DISCUSSION

Synthesis and Characterization

The synthetic route to the polymers was given in Scheme 1. The preparation of compound 1 was presented in the Supporting Information. 4-Bromophenylpyrrole (compound **S1**), the important starting material, was synthesized from 2,5dimethoxy THF and 4-bromoaniline in high yield, then 4-bromophenylpyrrole-2-carbaldehyde (compound **S2**) was obtained through the normal Vilsmeier reaction, which reacted with compound S3 under Wittig-Hornor reaction to yield compound S4. Again, by another Vilsmeier reaction, an aldehyde group was introduced to the pyrrole ring. Then, under the normal palladium-catalyzed Suzuki coupling of compound 1 and 2,2'-(9,9-dihexyl-9H-fluorene-2,7-diyl)bis (4,4,5,5-tetramethyl-1,3,2-dioxaborolane), the bisaldehyde 2 was obtained with fluorene moiety as the isolation moieties. Thus, in this reaction, various aromatic rings could be incorporated as the isolation moieties, and in this article, we chose fluorene as the example. The Wittig-Horner-Emmons olefination reaction between compound 2 and the required bisphosphonates with t-BuOK as catalyst, were chosen to synthesize polymers **P1-P3**. By using this approach, various bisphosphonates containing different electron-donating or electron-withdrawing groups could be conveniently introduced into the polymers to tune their optical properties.

The purified polymerization products gave satisfactory spectroscopic data corresponding to the expected molecular structures. They were soluble in common organic solvents such as THF, chloroform, DMF, and DMSO. The strong peak of the aldehyde group in monomer 2 appeared at about 1660 cm^{-1} in its FTIR spectroscopy (Supporting Information) Fig. S1). Also, in the FTIR spectra of the polymers, the peak around 1660 cm⁻¹ could be observed due to the presence of some terminal aldehyde groups (Supporting Information Fig. S2). The same phenomenon could be seen in their ¹H NMR spectra (Supporting Information Figs. S3-S5). All the polymers exhibited very good thermal stability, and their initial decomposition temperatures were above 320 °C under argon, where over 95% of their mass was retained (Supporting Information Fig. S6 and the detail data shown in Table 1). The molecular weights of P1-P3 were determined by GPC with THF as an eluent and polystyrene standards as calibration standards. As shown in Table 1 and Experimental section, these three polymers possessed different molecular weights, and from P1 to P3, the molecular weights increased. This should be ascribed to the different monomer structure of one of the compounds 3-5.

One-photon Physical Properties

The UV-Vis absorption spectra of the polymers in THF at dilute concentration were shown in Figure 1, and the data were summarized in Table 1. The absorption maximum (λ_{max}) of polymer **P2** was located at 461 nm, which was similar to the corresponding small molecules shown in Chart 3, indicating that the fluorene unit together with the two phenyls as the isolation moieties would inhibit the π stacking of the conjugation systems efficiently. When the conjugation bridge changed from 1,4-dimethoxyphenylene to fluorenylene one, the λ_{max} value of **P1** blue-shifted to 410 nm. This was reasonable. While the larger planar structure of the fluorenylene unit gave the effective charge transfer from the

TABLE 1	Some	Characterization	Data of	Polymers
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Polymers	Yield (%)	<i>M</i> _w (×10 ⁴) ^a	$M_{\rm w}/M_{\rm n}^{\rm a}$	λ ^{abs} (nm) ^b	λ ^{abs} (nm) ^c	λ ^{em} (nm) ^d	λ ^{em} (nm) ^e	λ ^{tp} (nm) ^f	Ф (%) ^g	σ (GM) ^h	<i>T</i> d (°C) ⁱ
P1	67.0	0.30	1.52	410	414	523	538	760	60.7	752	330
P2	61.0	0.77	1.57	461	460	559	589	760	39.3	1114	368
P3	73.2	2.47	1.88	508	518	640	716	760	13.3	1869	323

^a Determined by GPC in THF on the basis of a polystyrene calibration.

 $^{\rm b}$ 1.0 $\,\times\,$ 10 $^{-6}\,$ M per repeating unit in THF, wavelength of maximum absorbance.

 d 1.0 \times 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 \times 10 $^{-5}$ M per repeating unit in THF, wavelength of maximum 2PA cross-sections.

 g Quantum yields in THF solution using fluorescein in water ($\Phi_{\text{F}}=$ 90%, pH = 11) as a standard.

^h TPA cross-sections, 1 GM (Göppert-Mayer) = 10^{-50} cm⁴ s photon⁻¹, the experimental uncertainty on σ_{max} is of the order of 10–15%.

 $^{\rm i}$ The 5% weight loss temperature of polymers detected by the TGA analyses under argon at a heating rate of 10 $^\circ C/min.$

 $^{^{\}rm c}$ Absorption spectra of polymers in thin film, wavelength of maximum absorbance.



FIGURE 1 UV–Vis spectra (left) and PL spectra (right) of the polymers in THF. Concentration: 1.0 μ M in repeating unit. Inset: Photographs of the polymers in THF (left) and fluorescence photographs of the polymers in THF (right) under UV illumination. From the left to right: **P1**, **P2**, and **P3**.

terminal donor groups to the π bridge, the 1,4-dimethoxyphenylene unit with two methoxy groups substituted on the phenyl ring could increase the electron density of the bridge and benefit the intramolecular charge transfer. Therefore, **P1** demonstrated blue-shifted absorption in comparison to **P2**. Replacement of the 1,4-dimethoxyphenylene unit of **P2** with 1,4-dicyanophenylene in **P3**, the λ_{max} value of **P3** further red-shifted to 508 nm, indicating that the cyano substitution on the phenyl act as the acceptor group and facilitated the charge transfer between the terminal donor group and the π system. This suggested that their UV-Vis absorption mainly reflected the strong intramolecular charge transfer effect.

The one-photon emission spectra of the polymers followed the same trend with the absorption spectra. While the conjugation bridge changed from fluorenylene to 1,4-dimethoxyphenylene, then to 1,4-dicyanophenylene, the emission maximum were located at 523, 559, and 640 nm, respectively, indicating that their emission range could be well tuned by adjusting the nature of the conjugation bridge moieties. The fluorescence quantum yields (Φ) of **P1-P3** were tested to be in the range of 0.13–0.60. The high Φ value of the polymer **P1** may be due to the excellent electron properties of triphenylamine and pyrrole and the effect of the isolation moieties. The relatively lower quantum yield of **P3** was probably caused by its lower energy of the emitting states, which might facilitate the nonradiative pathways. As the polymers emitted different fluorescent color with relatively higher quantum yields, they might be used in organic light-emitting devices.

Figure 2 shows the optical properties of these polymers in the solid state, with the corresponding data summarized in Table 1. The trend of the solid-state spectra was similar to their solution ones; however, the spectra were red-shifted at different degrees. Generally, the conjugated systems became



FIGURE 2 Normalized solid-state absorption spectra (left) and normalized solid-state photoluminescence spectra (right) of the polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]



FIGURE 3 Two-photon absorption cross-section (σ) of polymers in THF.

more planar in the solid state. This led to an increase in the effective conjugation length and the red shifted absorption and photoluminescence (PL) spectra, in comparison with those in solutions. Unlike the little changes in their maximum absorption wavelengths, their maximum emission wavelengths red-shifted at a larger degree: P3 exhibited the emission wavelength as large as 76 nm, while those of P1 and P2 were 15 and 30 nm, respectively, although the aromatic rings in the three polymers changed from the big one of fluorene moieties in P1 to much smaller benzene rings in P2 and P3. Analyzing the results carefully, it was seen that from P1 to P3, the molecular weights increased, indicating the possible increase in π - π stacking among the long polymer chains, which might account for the increased redshifted emission. The little change of P1 from the solution to the solid film partially indicated the hindrance effect of the possible aggregation derived from these types of polymers. Also, no matter the large red-shifted maximum emission wavelengths of the three polymers, the curve of their emission spectra in the solid state did not change much in comparison with those in solutions, and the shoulder emissions of the π - π aggregation were not so obvious.

Two-Photon Absorption Properties

The TPA cross-sections (σ) were determined with the twophoton-induced fluorescence measured technique by using femtosecond laser pulses, which could avoid possible complications due to the excite-state excitation. In all cases, the output intensity of TPEF was linearly dependent on the square of the input laser intensity, thereby confirming the nonlinear absorption. Moreover, the one-photon emission and TPEF spectra overlapped with each other, indicating that the emission occurred from the same excited states, regardless of the mode of excitation. The TPA spectra of the polymers in THF were presented in Figure 3, and the data were collected in Table 1. The σ_{max} value gradually increased in the order of **P1** < **P2** < **P3**, reaching a maximum value of 1869 GM for **P3** per repeating unit. The main difference in these polymers was the core of the π bridge, the results suggested that the 1,4-dicyanophenylene group played a crucial role for the enhancement of σ values, and the different types of the conjugation bridge might involve different types of states on two-photon excitation. The smaller energy gap of **P3** would give the higher probability of two-photon excitation, disclosing that the strategy through the incorporation of the cyano substitution on the conjugation bridge to form a large π system with D- π -A- π -D backbone in the repeating unit could be an effective approach to enhance the σ values.

In addition, the electron-rich ring of pyrrole could act as the auxiliary donor, which made the structure of the repeating unit further change into the D-D'-A-D'-D type, and benefit the intramolecular charge transfer between the conjugation bridge and the two end groups. The *N*-arylpyrrole group in the polymers was also helpful to TPEF, which might make the conjugated polymers in good arrangement and avoid the loss of the energy by π - π stacking, and the branched aromatic rings linked to pyrrole ring through carbon-nitrogen bond might have the effective electronic coupling to the backbone, and enhance the σ value.

CONCLUSIONS

We have synthesized three novel conjugated polymers bearing *N*-arylpyrrole as conjugated bridge and isolation moieties by Wittig-Horner-Emmons olefination reaction. All the polymers exhibited good solubility, and their optical properties could be subtly tuned by different types of the conjugation bridges in repeating units. Thanks to the good electron properties of triphenylamine and pyrrole, and in the presence of the isolation moieties, all the polymers emitted strong fluorescence and possessed relatively higher quantum yields. They demonstrated strong TPA properties, and the maximal σ was 1869 GM for **P3** per repeating unit, indicating that the incorporation of the electron-rich pyrrole ring and the withdrawing 1,4-dicyanophenylene moiety into the conjugated system to form D–D'–A–D'–D structure was an effective approach for the enhancement of σ values.

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