Poly(1,4-diketo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole-*alt*−3,6-carbazole/2,7-fluorene) as High-Performance Two-Photon Dyes

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ABSTRACT: This article reports the synthesis, one- and two-photon absorption, and excited fluorescence properties of poly(1,4-diketo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole-*alt*-*N*-octyl-3,6-carbazole/2,7-fluorene) (**PDCZ**/**PDFL**). **PDCZ** and **PDFL** are synthesized by the Suzuki cross-coupling of 2,5-dioctyl-1,4-diketo-3,6-bis(*p*-bromophenylpyrrolo[3,4-*c*]pyrrole and *N*-octyl-3,6-bis(3,3-dimethyl-1,3,2-dioxaborolan-2-yl)carbazole or 2,7-bis(3,3-dimethyl-1,3,2-dioxaborolan-2-yl)fluorene and have number-average molecular weights of 8.5×10^3 and 1.14×10^4 g/mol and polydispersities of 2.06 and 1.83, respectively. They are highly soluble in common organic solvents and emit strong orange one- and two-photon excited fluorescence (2PEF) in THF solution and exhibit high light and heat stability. The maximal two-photon absorption cross-sections (δ) measured in THF solution by the 2PEF method using femtosecond laser pulses are 970 and 900 GM per repeating unit for **PDCZ** and **PDFL**, respectively. These 1,4-diketo-pyrrolo[3,4-*c*]pyrrole-containing polymers with full aromatic structure and large δ will be promising high-performance 2PA dyes applicable in two-photon science and technology. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 944–951

KEYWORDS: conjugated polymers; synthesis; photochemistry; two-photon absorption; high performance polymers

INTRODUCTION Two-photon dyes have potential applications in three-dimensional (3D) fluorescence imaging, optical power limitation, up-conversion lasing, 3D optical data storage, 3D microfabrication, and photodynamic therapy, which has stimulated much interest in the design, synthesis, and characterization of organic compounds exhibiting two-photon absorption (2PA) properties.[1,2] The most frequently investigated structural motifs are donor–acceptor–donor, donor–π-bridge–acceptor, donor–π-bridge–donor type molecules, macrocycles, dendrimers, multibranched compounds, and polymers. It has been revealed that 2PA cross-sections (δ) increase with the donor/acceptor strength, conjugation length, molecular dimensionality, and the planarity of the π-center.[1,2] With the optimization of structure and composition, a large number of conjugated molecules exhibiting large δ (>1000 GM) have been prepared. However, most of them are C=C and C≡C bond-containing conjugated organic molecules, which are subject to photo- and heat-instability and impair the efficiency and lifetime of materials since the primary causes of photochemical instability for optical dyes are the photooxidation and photoisomerization of the C=C bond.[3,4] Moreover, compared with extensively studied small molecular 2PA chromophores, light- and heat-stable-conjugated polymers with large δ are still scarce. In the past 15 years, 2PA properties of most typical conjugated polymers, such as poly(9,9-dialkylfluorene), poly(*p*-phenyleneethynylene), ladder-type poly(*p*-phenylene), poly[1,6-bis(3,6-dihexadecyl-*N*-carbazol-yl)-2,4-hexadiyne], and poly(phenylenevinylene)s have been measured using z-scan technique or nonlinear transmission method to show δ >10,000 GM.[5–9] However, these δ values are overestimated by roughly 2–3 orders because of the existence of excited-state absorption and thermal lens effects,[1,2,6] thus the real δ values of these traditional conjugated polymers are rather low (generally less than 100 GM per repeating unit) in terms of two-photon excitation fluorescence (2PEF) method. Therefore, there is still a considerable demand for polymeric fluorophores with fully aromatic structure and exhibiting high light and heat stability and large δ at present.

1,4-Diketo-pyrrolo[3,4-*c*]pyrrole (DPP) derivatives represent a class of brilliant red and strongly fluorescent high-performance pigments that have exceptional light, weather, and heat stability. Although DPP-containing conjugated polymers have been extensively synthesized and used as highly luminescent, electroactive, and photoactive materials in optical and optoelectronic fields,[10–15] the reports on their 2PA properties are still rare.[16,17] Recently, we and others have

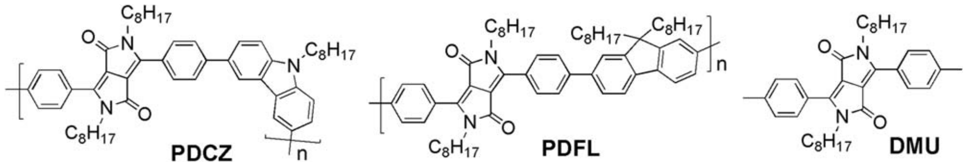


CHART 1 Structures of DPP-containing alternating copolymers (**PDCZ** and **PDFL**) and the model compound of DPP repeating unit (**DMU**) studied here.

demonstrated that DPP could be used as efficient π-center to construct the conjugated molecules exhibiting large δ,[16–18] and those monoalkylated derivatives also show one- and two-photon fluorescence sensing selectively to fluoride anion.[19,20] To further develop new DPP-based 2PA polymers, in this work, we have synthesized two simple fully aromatic DPP-containing co-polymers, poly(1,4-diketo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole-*alt*-*N*-octyl-3,6-carbazole/2,7-fluorene) (**PDCZ**/**PDFL**, Chart 1) to investigate their 2PA properties by the 2PEF method using femtosecond laser pulses. It is well known that 3,6-carbazole and 2,7-fluorene units have strong electron-donating and conjugation-extending abilities, respectively, which should permit a comparable investigation on effect of the co-polymeric units on the optical properties. For the sake of comparison, 2,5-dioctyl-3,6-di-*p*-tolyl-pyrrolo[3,4-*c*]pyrrole-1,4-dione (**DMU**, Chart 1) is also synthesized and used as the model compound of DPP repeating unit. It should be noticed that the one-photon excitation and electroluminescence properties of **PDCZ** and **PDFL** homologs have been investigated by Tieke and coworkers.[13] We now report that the two simple DPP-containing copolymers show high light and heat stability, and increasing both the donor strength and the conjugation length can greatly enhance their δ values.

EXPERIMENTAL

Materials

2,5-Dioctyl-1,4-diketo-3,6-bis(bromophenyl)pyrrolo[3,4-*c*]pyrrole (**DPP-Br**),[18] *N*-octyl-3,6-dibromocarbazole,[21] and 9,9-dioctyl-2,7-dibromofluorene[22] were from our previous works. $Pd(PPh_3)_4$, $(C_4H_9)_4NBr$, *n*-butyllithium, trimethylborate, and iodobenzene were purchased from Energy Chemical, China, and used without further purification.

Other chemicals were of analytical grade and were obtained commercially from available resources. Tetrahydrofuran (THF) was distillated over metallic sodium before use.

Synthesis of 3,6-Bis(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-N-octylcarbazole

A solution of *N*-octyl-3,6-dibromocarbazole (2.21 g, 5.1 mmol) in THF (50 mL) was added dropwise 1.6 M *n*-butyllithium in hexane (7.0 mL, 11.2 mmol) over 10 min at −78 °C under dry nitrogen. After stirring for 30 min at that temperature, trimethylborate (3.13 g, 30.1 mmol) was added into the mixture and then stirred for additional 30 min at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight and added 1 M HCl (50 mL). The organic phase was separated using ether, washed with brine, and dried over $MgSO_4$. After the solvent was removed, the residue was dissolved into THF and then added to hexane. The resulting white precipitate was collected by filtration and washed with hexane twice and dried in vacuum. This intermediate (1.3 g) was mixed with toluene (50 mL) and 2,2-dimethylpropane-1,3-diol (1.1 g, 10.6 mmol) and refluxed for 4 h, and the water produced was removed using a Dean–Stark trap. The organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the residue was re-crystallized from hexane to give the product as white solids (1.34 g, 52.3% yield).

^1H NMR (500 MHz, $CDCl_3$, δ): 8.65 (s, 2H), 7.89 (d, $J = 8.0$ Hz, 2H), 7.37 (d, $J = 8.5$ Hz, 2H), 4.29 (t, $J = 6.0$ Hz, 2H), 3.83 (s, 8H), 1.85 (m, 2H), 1.26 (m, 10H), 1.06 (s, 12H), 0.95 (t, $J = 6.0$ Hz, 3H); anal. calcd (%) for $C_{30}H_{43}B_2NO_4$: C, 71.59; H, 8.61; B, 4.30; N, 2.78; O, 12.72; found: C, 71.68; H, 8.63; N, 2.73.

2,7-Bis(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-9,9-dioctylfluorene

n-Butyllithium (7.0 mL of a 1.6 M solution in hexane, 11.2 mmol) was added dropwise into a solution of 9,9-dioctyl-2,7-dibromofluorene (2.75 g, 5.0 mmol) in THF (60 mL) at −78 °C under dry nitrogen. After stirring for 30 min, the mixture was added promptly trimethylborate (5.2 g, 50 mmol) and stirred for additional 1 h at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight and then added 1 M HCl (80 mL). The organic phase was separated using ether, washed with brine, and dried over $MgSO_4$. After the solvent was removed, the residue, without further purification, was refluxed with 2,2-dimethylpropane-1,3-diol (1.2 g, 11.5 mmol) in toluene for 6 h, meanwhile, the water produced was removed using a Dean–Stark trap. After cooling to room temperature, the mixture was washed with brine and dried over $MgSO_4$. The solvent was removed by rotary evaporator, and the residue was passed through a short silica gel column using ethyl acetate/petroleum ether (4/1) as the eluent and re-crystallized from THF/hexane (1/5) to give the product as white solids (1.12 g, 36.4% yield).

^1H NMR (500 MHz, $CDCl_3$, δ): 7.79 (d, $J = 7.0$ Hz, 2H), 7.75 (s, 2H), 7.71 (d, $J = 7.5$ Hz, 2H), 3.82 (s, 8H), 2.00 (m, 4H), 1.02–1.27 (m, 36H), 1.06 (s, 12H), 0.83 (t, $J = 6.0$ Hz, 6H); anal. calcd (%) for $C_{39}H_{60}B_2O_4$: C, 76.23; H, 9.84; B, 3.52; O, 10.41; found: C, 76.31; H, 9.79.

Poly(2,5-dioctyl-1,4-diketo-3,6-di(phenyl)pyrrolo[3,4-c]pyrrole-alt-N-octyl-3,6-carbazole)

DPP-Br (0.35 g, 0.522 mmol), 3,6-bis(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-*N*-octylcarbazole (**CZB**) (0.263 g, 0.522 mmol), $Pd(PPh_3)_4$ (0.013 g, 0.011 mmol), and K_2CO_3 (1.22 g, 8.83 mmol) were added into the mixture of toluene (7 mL) and water (7 mL) under nitrogen. The resulting mixture was refluxed under stirring and nitrogen protection for 48 h. Then 0.025 g of **CZB** (0.05 mmol) in toluene (0.5 mL) was added by a syringe, and reaction was continued for 6 h; subsequently, 0.15 g of iodobenzene (0.735 mmol) in toluene (0.5 mL) was added, and the reaction mixture was refluxed for additional 6 h. After cooling, 100 mL of chloroform was added, and the organic phase was washed with water and dried over $MgSO_4$. The filtrate was passed through a Celite pad to remove the residual catalysts. The solution obtained was concentrated to 20 mL and then poured into 100 mL of ethanol and stirred for 30 min. The solid obtained by filtration was extracted with acetone in a Soxhlet apparatus for 10 h. After drying, 0.22 g of dark red solids was obtained (53.5% yield).

Poly(2,5-dioctyl-1,4-diketo-3,6-di(phenyl)pyrrolo[3,4-c]pyrrole-alt-9,9-dioctyl-2,7-fluorene)

This polymer was prepared as described for **PDCZ** except that 2,7-bis(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-9,9-dioctylfluorene (**FB**) was used instead of **CZB**. After drying, 0.28 g of dark red solids was obtained (59.7% yield).

2,5-Dioctyl-1,4-diketo-3,6-di(p-tolyl)pyrrolo [3,4-c]pyrrole

To a stirring suspension of 3,6-bis(4-methyl-phenyl)pyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)-dione (0.82 g, 2.6 mmol) in DMF (30 mL), potassium *tert*-butoxide (1.2 g, 10.6 mmol) was added at room temperature under N_2. The resulting mixture was stirred for 30 min and then 1-bromooctane (1.64 g, 8.6 mmol) was added slowly. After stirring for additional 1 h at room temperature, the mixture was heated to 60 °C and stirred overnight. The cooled mixture was poured into 400 mL of water and stirred for 1 h. The solid obtained by filtration was purified by flash column chromatography using DCM/ethyl acetate = 20/1 as the eluent. An orange solid was obtained (0.88 g, 62.5% yield).

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.71 (d, $J = 8.0$ Hz, 4H), 7.32 (d, $J = 8.0$ Hz, 4H), 3.73 (t, $J = 7.5$ Hz, 4H), 2.45 (s, 6H), 1.58 (m, 4H), 1.23 (m, 20H), 0.84 (t, $J = 7.0$ Hz, 6H); anal. calcd (%) for $C_{36}H_{48}N_2O_2$: C, 79.96; H, 8.95; N, 5.18; O, 5.92; found: C, 79.88; H, 8.97; N, 5.21.

Measurements

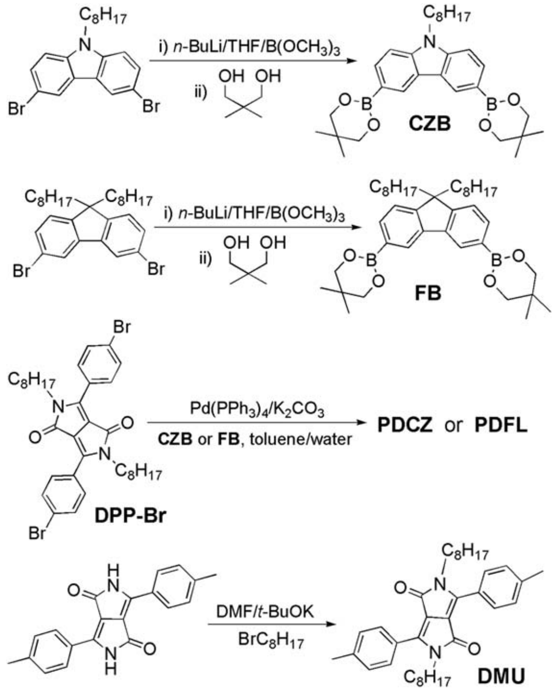
^{1}H NMR spectra were recorded on a Bruker-AC500 (500 MHz) spectrometer in $CDCl_3$. The ELEM. ANAL was performed on Perkin–Elmer 2400. Molecular weights were determined using GPC (Waters 1515 HPLC) equipped with calibrated styragel columns versus commercially available polystyrene standards with THF as an eluent. UV–visible absorption spectra were obtained on a Hitachi U-4100 spectrophotometer. Fluorescence emission spectra were performed on a Hitachi F-4600 spectrophotometer. The fluorescence quantum yield (Φ) was determined in THF at room temperature by the dilution method using rhodamine B in methanol as the reference.[23] Optically dilute THF solutions of DPP derivatives, and MeOH solution of the rhodamine B standard were prepared in 1 cm path length quartz cuvettes with absorbances <0.1. Polymer film for absorption and emission spectra was prepared by spin-coating the polymer solution in THF (15 mg/mL) on a quartz glass plate. The DSC analysis and the TGA were performed under N_2 atmosphere (50 mL/min) on a NETZSCH DSC 204F1 and a NETZSCH 209F1 thermogravimetric analyzer at heating rates of 10 °C/min (DSC) and 20 °C/min (TGA), respectively.

2PA cross-sections (δ) were measured with the two-photon-induced fluorescence (TPEF) method using femtosecond laser pulses as described before by us and others.[16,18,24,25] The excitation light source was a mode-locked Ti:sapphire femtosecond laser (Spectra-Physics, Tsunami 3941, 700–910 nm, 80 MHz, <120 fs) pumped by a compact cw prolite diode laser (Spectra-Physics, Millennia Pro 5S). The fluorescence signal was recorded by spectrofluorometer (Ocean Optics, USB2000). Samples were dissolved in THF at a concentration of 1.0×10^{-5} M in repeating unit, and the TPEF intensity was measured at 710–870 nm and compared under the same measurement conditions using Rhodamine B in methanol (1.0×10^{-5} M) as the reference.[26] The δ of sample (δ_s) was calculated using the equation: $\delta_s = [(S_s\Phi_r n_r^2 c_r)/(S_r\Phi_s n_s^2 c_s)]\delta_r$. The subscripts "s" and "r" indicate the sample and reference molecules, respectively. S is the integral area of the TPEF; Φ is the fluorescence quantum yield; n is the refractive indices of the solvents for the sample and reference; and c is the number density of the molecules in solution. δ_r is the δ of the reference molecule.

RESULTS AND DISCUSSION

Synthesis

The synthetic route for **PDCZ**, **PDFL**, and **DMU** is shown in Scheme 1. The monomers carbazole-diboronic ester (**CZB**), fluorene-diboronic ester (**FB**), and 2,5-dioctyl-1,4-diketo-3,6-bis(bromo-phenylpyrrolo[3,4-*c*]-pyrrole (**DPP-Br**) were prepared according to the known procedures. The Suzuki couplings of **DPP-Br** and **CZB** or **FB** in a mixture of 2 M K_2CO_3 and toluene with $Pd(PPh_3)_4$ as catalyst afforded the corresponding full aromatic alternating copolymers **PDCZ** and **PDFL**. The model compound of DPP repeating unit (**DMU**) was synthesized by *N*-alkylation of commercially available 3,6-di(*p*-methyl-phenyl)pyrrolo[3,4-*c*]-pyrrole-1,4(2H,5H)dione with 1-bromooctane in DMF using *t*-BuOK as catalyst. These compounds are all highly soluble in common organic solvents such as dichloromethane, toluene tetrahydrofuran (THF), and chloroform. The number-average molecular weight (M_n) estimated by gel permeation chromatography (GPC) against polystyrene standard with THF as eluent is 8.5×10^3 g/mol with a polydispersity of 2.06 for **PDCZ** and 1.14×10^4 g/mol with a polydispersity of 1.83 for **PDFL**, respectively (Table 1). It has been shown that, with regard to PPV type polymers, the changes in electronic properties caused by increasing the



SCHEME 1 Synthetic route of PDCZ, PDFL, and DMU.

conjugated length saturate at five to seven repeating units.[27] The average numbers of repeating units of the as-synthesized polymers are estimated to be approximately 10–13. Therefore, the chain lengths of the as-synthesized polymers are sufficient to represent the optoelectronic properties of extended π-systems even if their M_n values might be overestimated, as observed in other conjugated polymers.[28]

Light- and Heat-Resistant Properties

Unlike arylenevinylene derivatives, DPP derivatives have exceptional light, weather, and heat stability. To test the light and heat stability of full aromatic copolymers **PDCZ** and **PDFL**, the polymer solutions are put into glass tubes and exposed to sunlight or irradiated with an ordinary light bulb (100 W) in air for 3 days. No changes are found in both absorption and emission spectra. The thermal properties are investigated with thermogravimetric analysis (TGA, under nitrogen or air) and differential scanning calorimetry (DSC, under nitrogen) and the corresponding data are summarized in Table 1. As shown in Figure 1 and Table 1, **PDCZ** and **PDFL** solids have similar but unobvious glass transitions at about 105 °C (as indicated by arrows in the inset of Fig. 1). TGA curves indicate that the two polymers have the onset decomposition temperatures around 310 °C in nitrogen (based on 5% weight loss). Noticeably, the onset decomposition temperatures of **PDCZ** and **PDFL** in air are still up to 279 and 290 °C, respectively, and there are hardly weight losses before 200 °C (Fig. 1). These results indicate that **PDCZ** and **PDFL** exhibit excellent light and heat stability in both inert and air atmospheres, which are fairly valuable for 2PA dyes.

Linear Absorption and One-Photon Excited Fluorescence Properties

The one-photon absorption and emission spectra of **PDCZ** and **PDFL** are investigated in both THF solutions and solid films, and the absorption and emission spectra of their DPP repeating unit analog **DMU** in THF solution are also recorded for comparison. Related spectroscopic data are summarized in Table 1. Figure 2 depicts the absorption and emission spectra of **PDCZ**, **PDFL**, and **DMU** in THF solutions. Although the absorption maxima of copolymers are red-shifted only by 7–9 nm related to that of **DMU** (Table 1), the long-wavelength absorption bands of **PDCZ** and **PDFL** are significantly broadened toward long-wavelength regions [Fig. 2(a)]. This indicates that the electronic states of DPP and carbazole or fluorene units are mixed to a large extent to render a strong intramolecular charge transfer (ICT). It is observed that the long-wavelength absorption bands of **PDCZ** and **PDFL** are very similar, implying that the ICT effect induced by strong electron-donating 3,6-carbazole is similar to that by strong conjugation-extending 2,7-fluorene in this system. The strong and similar ICT effect in the two copolymers is further evidenced by the fluorescence emission spectra [Fig. 2(b)]. The emission spectra of **PDCZ** and **PDFL** in THF solutions are very same in both shape and position but red-shifted significantly by about 55 nm compared to that of **DMU** (Table 1). The solution fluorescence quantum yields (Φ) of **PDCZ**, **PDFL**, and **DMU** in THF measured by dilute solution method using Rhodamine B as the reference are 28.6, 43.4, and 61.1%, respectively. Figure 3 shows the

TABLE 1 Molecular Weight, Optical Properties, and Thermal Analysis Data of **PDCZ** and **PDFL**

Cpds	M_n/PD[a]	λ_{max}[b] Soln/Film	λ_{em}[c] Soln/Film	Stokes-Shift[d] Soln/Film	Φ (%)[e]	δ_{max}[f] (GM)	T_g/°C[g]	T_d/°C[h] in N_2/Air
PDCZ	8,540/2.06	502/506	583/631	81/125	28.6	970	103	307/279
PDFL	11,400/1.83	500/505	579/600	79/95	43.4	899	105	312/290
DMU	540/–	493/nd[i]	526/nd	33/-	61.1	107	nd	nd

[a] Number-average molecular weight (M_n) and polydispersity (PD) measured by GPC using THF as the eluent.

[b] Peak wavelength (nm) of the lowest energy one-photon absorption band in THF solutions (soln) and solid films (film).

[c] Peak wavelength (nm) of one-photon emission spectra.

[d] Stokes shift in nanometer.

[e] Fluorescence quantum yield in THF.

[f] Maximal two-photon absorption cross section in 10^{-50} cm^4 s/photon (GM).

[g] Glass transition temperature at a heating rate of 10 °C/min.

[h] Thermal decomposition (5% weight losses) temperature under nitrogen or air atmosphere at a heating rate of 20 °C/min.

[i] Not determined.

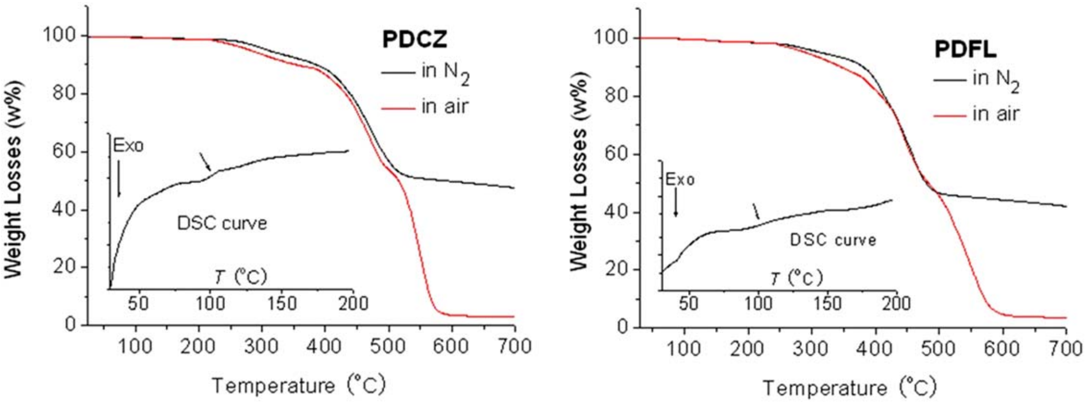


FIGURE 1 TGA thermogram (heating rate 20 °C/min) and DSC traces (inset, heating rate 10 °C/min) of **PDCZ** and **PDFL**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

absorption and emission spectra of **PDCZ** and **PDFL** in solid films. The absorption spectra of PDCZ and PDFL in solid films are similar to those in solutions [Fig. 2(a)], whereas the emission spectra in solid films are much broader and red-shifted significantly by 48 and 21 nm for PDCZ and PDFL, respectively, relative to those in solutions [Fig. 2(a) and Table 1]. This suggests the presence of aggregation of the polymer main chains in the solid states arising from the inherent rigid nature of their backbones and the higher planarity and polarity of heterocyclic DPP moieties. The broader emission spectrum and larger Stokes shift observed for **PDCZ** than **PDFL** imply that there are stronger interactions between transition moments of nearest neighbor **PDCZ** molecules in the solid sates. The similar phenomenon has been observed for other narrow-band-gap heterocycle-containing copolymers.

Two-Photon Absorption and Excited Fluorescence

We used two-photon excited fluorescence measurement technique to investigate the two-photon properties of the two copolymers and their DPP repeating unit analog in THF solutions. The femtosecond laser pulses (mode-locked Ti:sapphire femtosecond laser, 120 fs, 80 MHz) were used, which could give reliable 2PA cross-sections (δ) and avoid possible complications due to the excited-state absorption and thermal lens effects.

To confirm the occurrence of nonlinear absorption, the two-photon excited fluorescence (2PEF) of **PDCZ** and **PDFL** is recorded under 820 nm excitation with changed input laser powers (60–180 mW). It has been confirmed that the copolymers have strong linear absorption before 600 nm, but no linear absorption in the spectral range of 600–1100 nm. Thus, if there undoubtedly is any fluorescence emission emerged from the polymer solutions under the irradiation with an 820 nm of laser pulses; it must not be from one-photon excitation. We have observed the fluorescence emission from the polymer solutions under different laser intensities, moreover, the fluorescence intensities are gradually increased with the input laser power (Fig. 4). To confirm the occurrence of nonlinear absorption, the relation plot between logarithmic output fluorescence intensity and logarithmic input laser power is drawn (Fig. 5). The slopes obtained by the linear fitting of the experimental data are 1.93 for **PDCZ** and 1.96 for **PDFL**, respectively, which are very close to power-law dependence and indicative of a two-

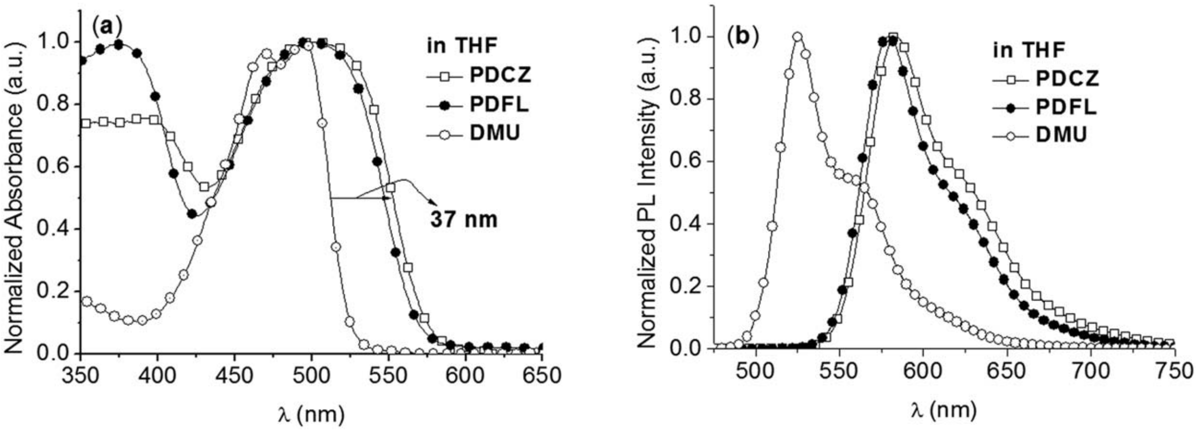


FIGURE 2 UV–visible absorption (a) and one-photon excited fluorescence (b) spectra of **PDCZ**, **PDFL**, and **DMU** in THF solutions at 1.0×10^{-5} M in repeating unit.

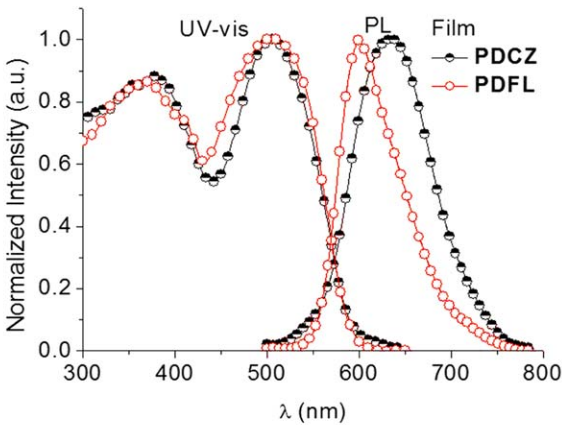


FIGURE 3 UV–visible absorption and one-photon excited fluorescence (PL) spectra of **PDCZ** and **PDFL** in film state. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

photon excitation process (Fig. 5). Figure 6(a) shows the one- and two-photon excitation fluorescence spectra. There is a good spectral overlap between the respective one- and two-photon excitation fluorescence whose peak emission wavelengths are the same as each other, indicating that the fluorescence emission occurs from the same excited states, regardless of the mode of excitation. Meanwhile, an obvious difference between one- and two-photon excited emissions is observed for both **PDCZ** and **PDFL** [Fig. 6(a)]. The 2PEF spectra are obviously narrower than the one-photon ones. However, it is not clear whether the two copolymers have up-conversion lasing properties, and further investigations are needed.

Figure 6(b) shows the two-photon excitation spectra of **PDCZ**, **PDFL**, and **DMU** in THF, and the relevant maximal δ ($\delta_{\max}$) are compiled in Table 1. The input laser power of 100 mW for **PDCZ** and **PDFL** and 150 mW for **DMU** is used, which fall within the power range of the two-photon excitation mode as shown in Figure 5. The available excitation

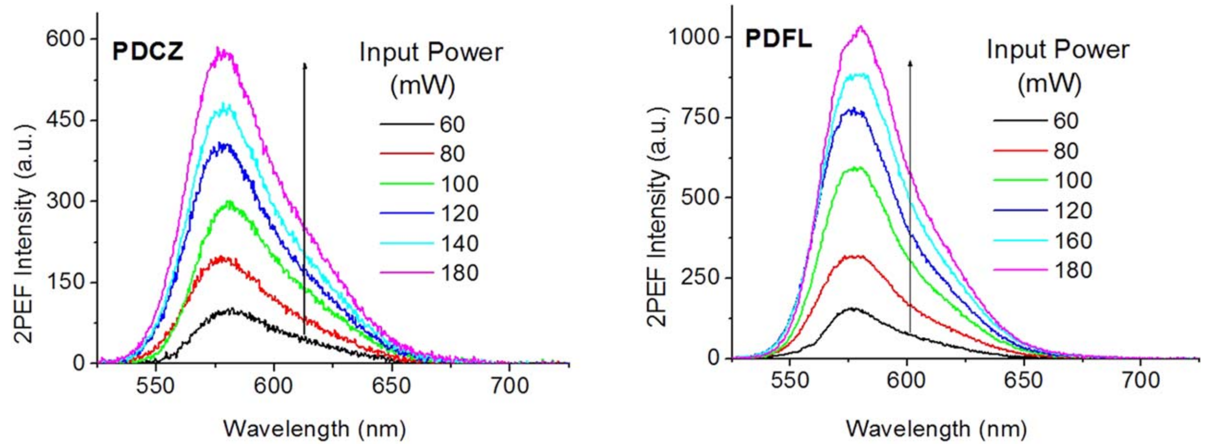


FIGURE 4 Two-photon excited fluorescence (2PEF) spectra of **PDCZ** and **PDFL** solutions in THF at 1.0×10^{-5} M in repeating unit under the excitation wavelength of 820 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

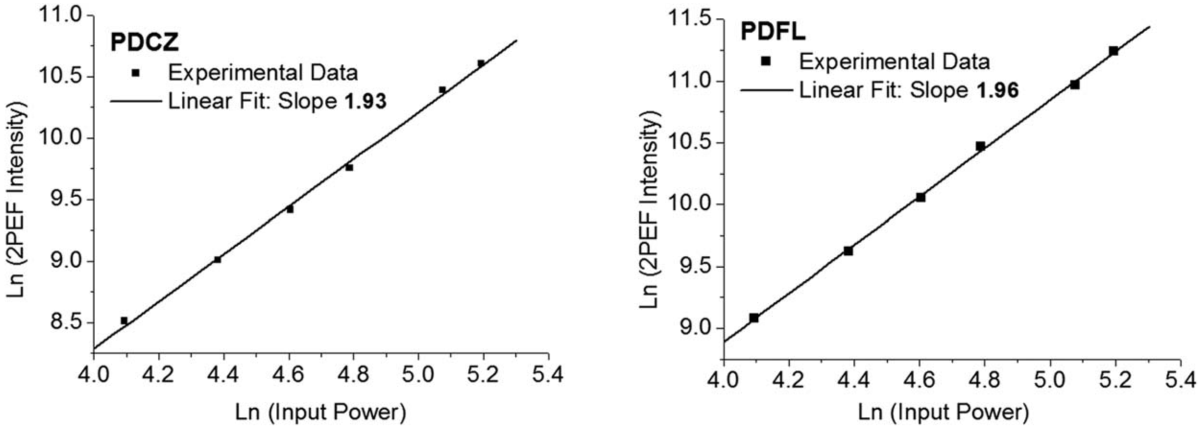


FIGURE 5 The dependence of output fluorescence intensity of **PDCZ** and **PDFL** solutions on the input laser power. Other conditions are same as Figure 4.

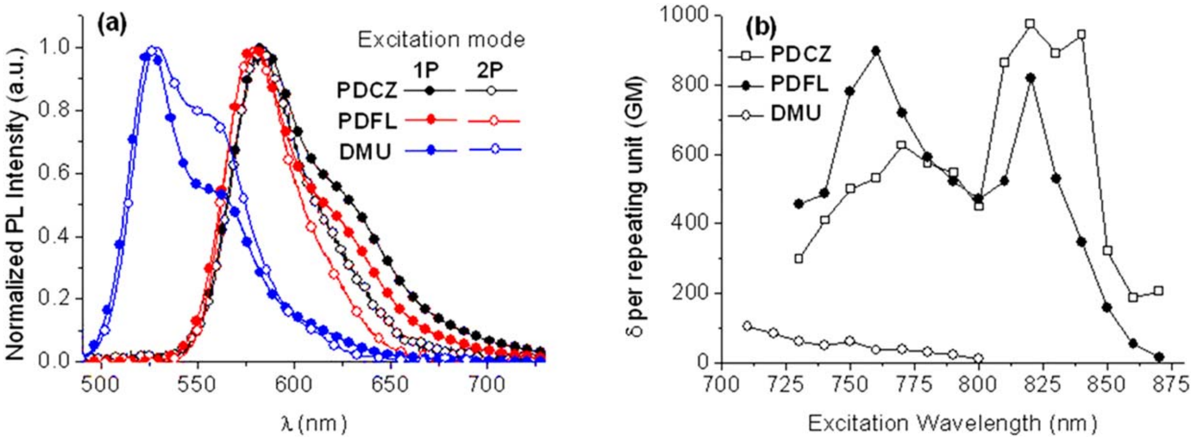


FIGURE 6 (a) Comparison between one-photon (1P) and two-photon (2P) excited fluorescence spectra. (b) Two-photon excitation spectra of **PDCZ**, **PDFL**, and their DPP unit analog **DMU** under input laser power of 100 mW for **PDCZ** and **PDFL**, and 150 mW for **DMU**. The concentration of 2PA dye is at 1.0×10^{-5} M in repeating unit. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

wavelength is in a range of 710–870 nm. It is shown that the 2PA band of **DMU** locates mainly short-wavelength region, and the absolute δ value is small although it is considerable in terms of molecular skeleton size. When extending linearly the molecular conjugation length or incorporating the strong electron-donating end-groups by copolymerization with 2,7-fluorene or 3,6-carbazole, respectively, the resulting copolymers **PDCZ** and **PDFL** exhibit greatly broadened and enhanced 2PA bands. The $\delta_{\max}$ values of **PDCZ** and **PDFL** are up to 970 and 899 GM per repeating unit, respectively, which are significantly larger than that of DPP repeating unit analog **DMU** and are also the largest among those fully aromatic conjugated polymers reported so far in terms of the TPEF measurement method. This clearly indicates that both extending the conjugation length and incorporating the strong electron-donating unit can significantly enhance δ of DPP-containing 2PA dyes. Moreover, extending the conjugation length and incorporating the strong electron-donating unit has same effectiveness in enhancing the δ of this system. The δ values of these simple fully aromatic conjugated polymers are larger than those of both their complex analogous and C≡C bond-bridged DPP–triphenylamine hyperbranched polymers.[16,17]

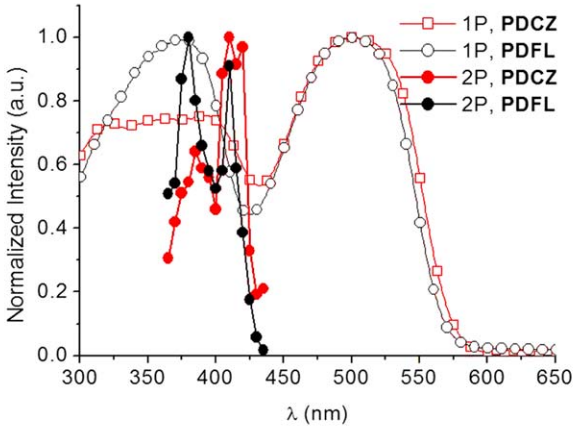


FIGURE 7 One-photon absorption (1P) and two-photon excitation (2P) spectra. The two-photon spectra are plotted against half the wavelength (twice the photon energy). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7 shows that the two-photon-allowed states are located at lower wavelength (higher energies) regions than their Franck–Condon states (one-photon allowed states) for both **PDCZ** and **PDFL**; moreover, there is no significant overlap between two allowed states in terms of the total absorption energy. These results imply that their one- and two-photon allowed states (selection rules) are different.

CONCLUSIONS

We have synthesized poly(1,4-diketo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole-*alt*-*N*-octyl-3,6-carbazole/2,7-fluorene) (**PDCZ/PDFL**) to demonstrate that simple DPP-containing conjugated copolymers show large δ. The $\delta_{\max}$ values of **PDCZ** and **PDFL** measured by TPEF method are up to 970 and 899 GM per repeating unit, respectively, the largest so far among fully aromatic conjugated polymers. **PDCZ** and **PDFL** having the similar large δ indicate that extending the conjugation length and incorporating the strong electron-donating unit have same effectiveness in enhancing the δ of this system. This work demonstrates once again that DPP is a novel and efficient π-center for the construction of high-performance 2PA dyes. DPP-containing fully aromatic conjugated polymers with large δ and high light and heat stability may ultimately find useful applications in two-photon science and technology.

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