

# Large Femtosecond Third-Order Nonlinear Optical Response in a Novel Donor–Acceptor Copolymer Consisting of Ethynylfluorene and Tetraphenyldiaminobiphenyl Units

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A novel donor–acceptor conjugated copolymer consisting of the electron-accepting moiety 2,7-diethynylfluorene and the electron-donating moiety tetraphenyldiaminobiphenyl (TPD), i.e., poly{(2,7-diethynyl-9,9-di-2-ethylhexylfluorene)-*alt-co*-[*N,N*-diphenyl-*N,N*-bis(4-phenyl)-1,1'-biphenyl-4,4'-diamine]} (TPD-PFE), and its cousins without the alkyne or TPD segments, namely, poly{(9,9-di-2-ethylhexyl-2,7-fluorene)-*alt-co*-[*N,N*-diphenyl-*N,N*-bis(4-phenyl)-1,1'-biphenyl-4,4'-diamine]} (TPD-PF) and poly(2,7-9,9-di-2-ethylhexylfluorenyleneethynylene) (PFE), were synthesized via Pd-catalyzed coupling reactions. The third-order nonlinear optical (NLO) properties of these polymers were characterized using a femtosecond time-resolved optical Kerr effect technique. The ultrafast second-order hyperpolarizability of TPD-PFE was estimated to be as large as  $4.5 \times 10^{-30}$  esu in the nonresonant region, larger than those of its counterparts. The electronic transitions of the fluorene-based polymers can be readily tuned by varying the nature of the co-units in the main chain, and the intrachain charge transfer between the electron-deficient and electron-excessive units can enhance the NLO properties of the polymers.

Conjugated polymers with delocalized  $\pi$  electrons are attractive candidates for potential applications in optical switching, computing, bistable elements, and logic devices because of their relatively low cost, fast nonlinear optical (NLO) response, large NLO susceptibility, and good processibility for multilayer integration into large-area devices.<sup>1</sup> Through the synthesis of intramolecular charge-transfer (CT) complexes, a significant enhancement of the optical nonlinearity in many CT systems has been theoretically predicted and experimentally explored.<sup>2,3</sup>

The large third-order nonlinear optical susceptibility  $\chi^{(3)}$ , good processibility, and excellent stability of poly-

(aryleneethynylene)s (PAEs) make them another class of prospective materials for NLO applications.<sup>4</sup> The third-order nonlinear optical effect of PAEs has been measured for a few systems, such as poly(phenyleneethynylene)s.<sup>5</sup> In general, aryleneethynylene is an interesting electron-accepting group because of the electron-withdrawing effect of the carbon–carbon triple bond.<sup>5a</sup> On the other hand, fluorene is a suitable arylene moiety because it is well-conjugated, electron-drawing, and easy to substitute with solubilizing groups.<sup>6</sup> Finally, the strong electron-donating ability of tetraphenyldiaminobiphenyl (TPD) makes it a well-known hole-transport material in the fabrication of small-molecule light-emitting diodes (LEDs).<sup>7</sup>

In the hope of combining both the good electron-accepting properties of 2,7-diethynylfluorene and the excellent electron-donating properties of TPD into a single main chain of polymer to enhance the third-order

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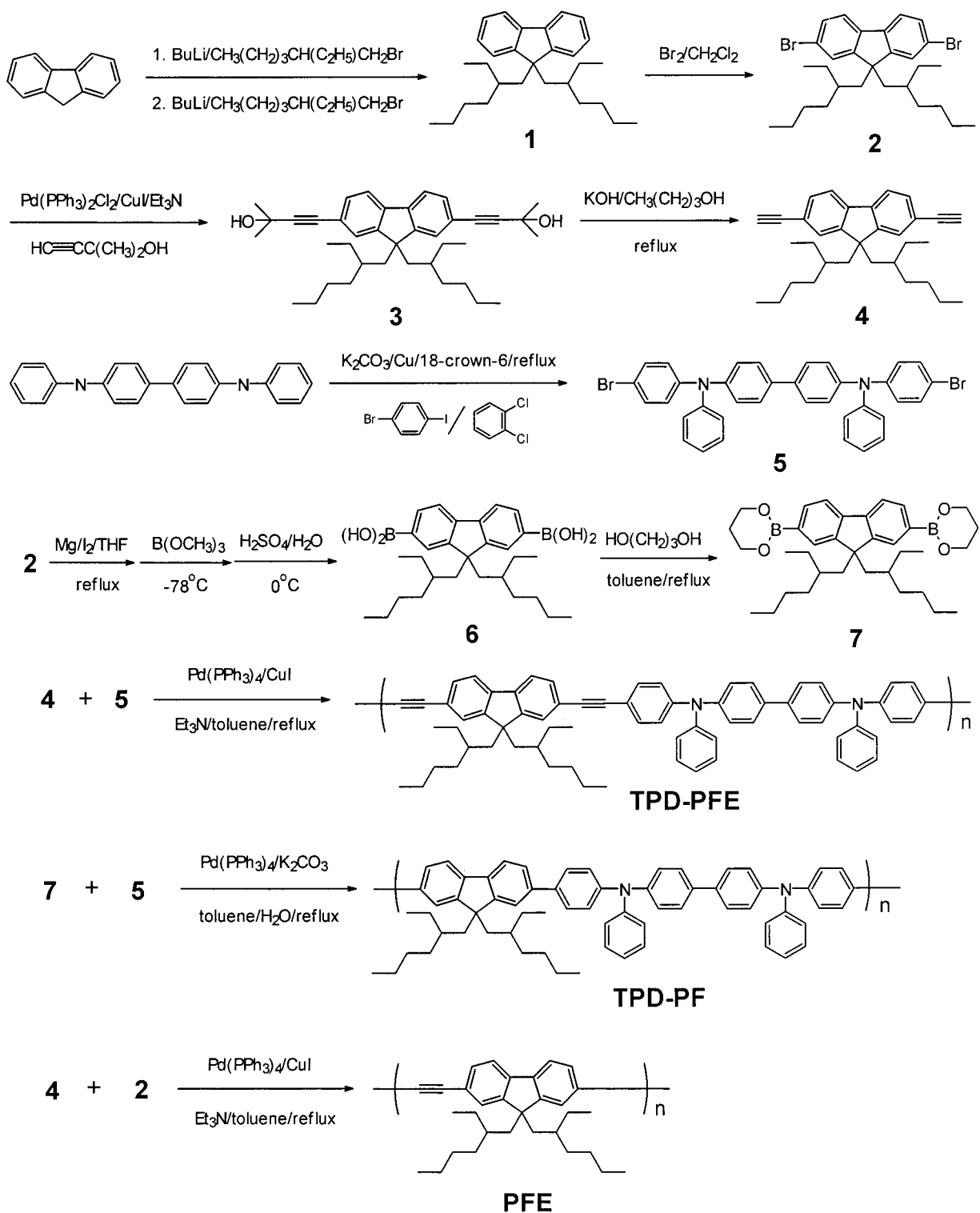
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## Scheme 1. Synthetic Route to the Three Polymers TPD-PFE, PFE, and TPD-PF



optical nonlinearity, we have synthesized a novel donor–acceptor copolymer containing these two functional segments via a Pd-catalyzed coupling reaction. In this article, we report the preparation of this  $\pi$ -conjugated polymer with an intrachain CT structure and discuss its NLO properties as measured using a femtosecond time-resolved optical Kerr effect (OKE) technique.

The synthetic route to three polymers is shown in Scheme 1. 2,7-Dibromo-9,9-di-2-ethylhexylfluorene (**2**) was synthesized (yield 81%) by a reaction of fluorene and 2-ethylhexylbromide using *n*-butyllithium in THF

according to the literature procedure,<sup>8</sup> followed by bromination of 9,9-di-2-ethylhexylfluorene (**1**) using excess bromine in CH<sub>2</sub>Cl<sub>2</sub> in the presence of iodine.<sup>9</sup> The palladium-catalyzed coupling of 2-methyl-3-butyn-2-ol with **2** in triethylamine generated 2,7-bis(3-hydroxy-3-methylbutynyl)-9,9-di-2-ethylhexylfluorene (**3**) (yield 85%),<sup>10</sup> which was converted to 2,7-diethynyl-9,9-di-2-

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ethylhexylfluorene (**4**) (yield 90%) by a base-promoted deprotection.<sup>11</sup> *N,N*-diphenyl-*N,N*-bis(4-bromophenyl)-1,1'-biphenyl-4,4'-diamine (**5**) was synthesized (yield 76%) by Ullmann reaction of *N,N*-diphenylbenzidine and 1-bromo-4-iodobenzene in *o*-dichlorobenzene in the presence of activated copper and the phase-transfer catalyst 18-crown-6.<sup>12</sup> The fluorene dibromide **2** reacted readily with magnesium in THF to form a difunctional Grignard reagent, which, when treated with trimethyl borate at  $-78\text{ }^{\circ}\text{C}$  followed by acidification, gave 9,9-di-2-ethylhexylfluorene-2,7-bis(boronic acid) (**6**) (yield 81%).<sup>13</sup> 9,9-Di-2-ethylhexylfluorene-2,7-bis(trimethylene boronate) (**7**) was prepared (yield 93%) by esterification of the diboronic acid (**6**) with trimethylene glycol.<sup>14</sup>

The copolymer poly{(2,7-diethynyl-9,9-di-2-ethylhexylfluorene)-*alt-co*-[*N,N*-diphenyl-*N,N*-bis(4-phenyl)-1,1'-biphenyl-4,4'-diamine]} (TPD-PFE) was prepared (yield 85%) by the palladium-catalyzed coupling condensation reaction between **4** and **5** in triethylamine and toluene at reflux for 48 h under nitrogen atmosphere.<sup>15</sup> For com-

parison, a homopolymer poly(2,7-9,9-di-2-ethylhexylfluorenyleneethynylene) (PFE) without TPD was also synthesized by the condensation reaction between **2** and **4** in a similar way (yield 82%).<sup>16</sup> Moreover, the copolymer poly{(9,9-di-2-ethylhexyl-2,7-fluorene)-*alt-co*-[*N,N*-diphenyl-*N,N*-bis(4-phenyl)-1,1'-biphenyl-4,4'-diamine]} (TPD-PF) without the carbon-carbon triple bond was also prepared (yield 92%) through a palladium-catalyzed Suzuki coupling reaction between **7** and **5** in toluene.<sup>17</sup> The chemical structures of the polymers were confirmed by  $^1\text{H}$  NMR and FT-IR spectroscopy and by elemental analysis.

The three fluorene-based polymers thus obtained are soluble in common organic solvents, such as chloroform, THF, and toluene. This is partially due to the 2-ethylhexyl side chain attached to the fluorene moiety. The molecular weights of these polymers were determined by gel permeation chromatography (GPC) with THF as the eluent and polystyrene as the standard. The weight-average molecular weight ( $M_w$ ) and polydispersity index ( $M_w/M_n$ ) of the three polymers are given in Table 1. TPD-PFE has a  $M_w$  of 17 600 with a  $M_w/M_n$  of 2.8, PFE has a  $M_w$  of 19 200 with a  $M_w/M_n$  of 2.5, and TPD-PF has a  $M_w$  of 9300 with a  $M_w/M_n$  of 2.2.

The thermal properties of the three polymers were determined by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC), and the onset decomposition temperature ( $T_d$ ) and glass transition temperature ( $T_g$ ) are summarized in Table 1. The decomposition temperatures of TPD-PFE, PFE, and

(10) Compound **3**: To a solution of **2** (2.74 g, 5 mmol) in dry triethylamine (40 mL) was added 2-methyl-3-butyn-2-ol (1.26 g, 15 mmol). After the solution was degassed with nitrogen for 30 min while stirring, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (70 mg, 0.10 mmol) and CuI (47.5 mg, 0.25 mmol) were added. The reaction mixture was then refluxed under nitrogen for 24 h. After the reaction was complete, the crude mixture was filtered at room temperature to remove triethylammonium bromide precipitate. The precipitate was rinsed with diethyl ether, and the combined filtrates were evaporated to dryness. The residue was purified by flash column chromatography (silica gel, 20% ethyl acetate in petroleum ether) to give compound **3** (2.36 g, 85%) as an orange oil. Anal. Calcd for C<sub>39</sub>H<sub>54</sub>O<sub>2</sub>: C, 84.42; H, 9.81. Found: C, 84.09; H, 9.98. MS (EI): *m/e* 555 (calcd for C<sub>39</sub>H<sub>54</sub>O<sub>2</sub> 554.85).  $^1\text{H}$  NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.66 (d, 2H), 7.43 (d, 2H), 7.30 (d, 2H), 2.26 (s, 2H), 1.96 (br, 4H), 1.66 (s, 12H), 1.27 (s, 2H), 0.92–0.65 (m, 22H), 0.54 (t, 6H).

(11) Compound **4**: A mixture of **3** (4.44 g, 8 mmol) and pulverized KOH (3.0 g, 50 mmol) in 1-butanol (50 mL) was refluxed under nitrogen with vigorous stirring for 2 h. The solution was transferred into a dropping funnel, and water was added. The organic layer was extracted with diethyl ether, dried over MgSO<sub>4</sub>, and evaporated to dryness. The residue was purified by flash column chromatography (silica gel, 10% ethyl acetate in petroleum ether) to give monomer **4** (3.15 g, 90%) as an orange oil. Anal. Calcd for C<sub>33</sub>H<sub>42</sub>: C, 90.35; H, 9.65. Found: C, 90.57; H, 9.68. MS (EI): *m/e* 438 (calcd for C<sub>33</sub>H<sub>42</sub> 438.69).  $^1\text{H}$  NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.64 (d, 2H), 7.33 (d, 2H), 7.23 (dd, 2H), 3.10 (s, 2H), 1.96 (br, 4H), 1.26 (s, 2H), 0.88–0.63 (m, 22H), 0.47 (t, 6H).

(12) Compound **5**: A mixture of *N,N*-diphenylbenzidine (1.68 g, 5 mmol), 1-bromo-4-iodobenzene (3.40 g, 12 mmol), K<sub>2</sub>CO<sub>3</sub> (2.76 g, 20 mmol), Cu (1.27 g, 20 mmol), and 18-crown-6 (1.32 g, 5 mmol) in *o*-dichlorobenzene (20 mL) was degassed with nitrogen for 30 min while stirring. The reaction mixture was then refluxed under nitrogen for 24 h. After the reaction was complete, the crude mixture was filtered. The solids were rinsed with CHCl<sub>3</sub>, and the combined filtrates were evaporated to dryness. The residue was purified by flash column chromatography (silica gel, 20% ethyl acetate in petroleum ether) to give monomer **5** (2.46 g, 76%) as a white solid. Anal. Calcd for C<sub>36</sub>H<sub>26</sub>N<sub>2</sub>Br<sub>2</sub>: C, 66.89; H, 4.05. Found: C, 66.55; H, 4.11. MS (FAB): *m/e* 646 (calcd for C<sub>36</sub>H<sub>26</sub>N<sub>2</sub>Br<sub>2</sub> 646.42).  $^1\text{H}$  NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.46 (m, 8H), 7.28 (m, 4H), 7.14 (m, 12H), 6.86 (d, 2H).

(13) Compound **6**: In a three-necked flask were charged **2** (5.5 g, 10 mmol), magnesium turnings (0.6 g, 25 mmol), and THF (20 mL) under nitrogen. The reaction was initiated by the addition of iodine (0.06 g). The resulting mixture was heated under reflux for 24 h. After being cooled to  $-78\text{ }^{\circ}\text{C}$ , a solution of trimethyl borate (2.8 mL, 25 mmol) in dry THF (10 mL) was added dropwise for 45 min. This reaction mixture was stirred at room temperature for 72 h, diluted with THF (40 mL), and added to a stirred mixture of crushed ice (200 g) and concentrated sulfuric acid (20 mL). The addition of diethyl ether (20 mL) and water (100 mL) facilitated the separation of the organic and aqueous layers. The aqueous layer was extracted repeatedly with diethyl ether (4  $\times$  50 mL), dried over MgSO<sub>4</sub>, and evaporated to dryness. The residue was recrystallized from acetone (20 mL) by the addition of hydrogen chloride (40 mL) to give a white solid (3.9 g, 81%). Mp: 219  $^{\circ}\text{C}$ . Anal. Calcd for C<sub>29</sub>H<sub>44</sub>O<sub>4</sub>B<sub>2</sub>: C, 72.83; H, 9.27. Found: C, 72.66; H, 9.17.  $^1\text{H}$  NMR (300 MHz, DMSO-*d*<sub>6</sub>),  $\delta$  (ppm): 8.26 (s, 4H), 7.92 (m, 2H), 7.80 (m, 2H), 7.70 (m, 2H), 1.95 (br, 4H), 1.20 (s, 2H), 0.79–0.58 (m, 22H), 0.42 (t, 6H). FT-IR (KBr),  $\nu$  (cm<sup>-1</sup>): 3447, 2958, 2926, 2857, 1728, 1608, 1464, 1421, 1351, 1324, 1123, 1075, 742.

(14) Compound **7**: In a three-necked flask were placed **6** (4.8 g, 10 mmol), trimethylene glycol (1.5 mL, 21 mmol), and toluene (60 mL), and the mixture was refluxed under nitrogen for 4 h. The solvent was distilled, and the residue was dissolved in diethyl ether (50 mL) and dried over magnesium sulfate. The solvent was evaporated to afford a pale yellow oil (5.2 g, 93%). Anal. Calcd for C<sub>35</sub>H<sub>52</sub>O<sub>4</sub>B<sub>2</sub>: C, 75.28; H, 9.39. Found: C, 75.66; H, 9.58.  $^1\text{H}$  NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.78 (d, 2H), 7.71 (d, 2H), 7.68 (d, 2H), 4.19 (t, 8H), 2.07 (t, 4H), 1.98 (d, 4H), 1.27 (s, 2H), 0.88–0.68 (m, 22H), 0.47 (t, 6H).

(15) TPD-PFE: A mixture of **5** (646 mg, 1.0 mmol) and **4** (438 mg, 1.0 mmol) in triethylamine (20 mL) and toluene (40 mL) was degassed for 30 min. Pd(PPh<sub>3</sub>)<sub>4</sub> (58 mg, 0.05 mmol) and CuI (10 mg, 0.05 mmol) were added. After the reaction mixture was refluxed under nitrogen for 48 h, it was filtered at room temperature to remove triethylammonium bromide precipitate. The salt was rinsed with diethyl ether, and the combined filtrates were evaporated to dryness. The residue was dissolved in a minimum amount of CHCl<sub>3</sub> and then poured into methanol to give a precipitate. The obtained solid was redissolved in CHCl<sub>3</sub> and reprecipitated from methanol, followed by Soxhlet extraction with the same solution for 24 h to give an orange powder (0.78 g, 85%). Anal. Calcd for (C<sub>69</sub>H<sub>66</sub>N<sub>2</sub>)<sub>n</sub>: C, 89.76; H, 7.20. Found: C, 89.24; H, 7.49.  $^1\text{H}$  NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.82–6.85 (m, 32H), 1.98 (br, 4H), 1.25 (s, 2H), 1.00–0.30 (m, 28H). FT-IR (KBr),  $\nu$  (cm<sup>-1</sup>): 2958, 2926, 2871, 2857, 1593, 1492, 1466, 1320, 1275, 820, 754, 697.

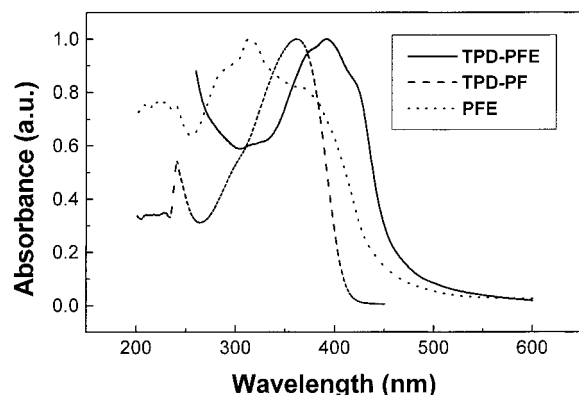
(16) PFE was prepared from **2** and **4** by a procedure similar to that of TPD-PFE. The product was isolated as a yellow powder in a yield of 82%. Anal. Calcd for (C<sub>31</sub>H<sub>40</sub>)<sub>n</sub>: C, 90.23; H, 9.77. Found: C, 89.51; H, 9.89.  $^1\text{H}$  NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.68 (d, 2H), 7.50 (dd, 4H), 1.95 (d, 4H), 1.25 (s, 2H), 1.00–0.40 (m, 28H). FT-IR (KBr),  $\nu$  (cm<sup>-1</sup>): 2959, 2926, 2872, 2857, 1645, 1606, 1464, 1379, 1262, 1097, 1026, 805, 741, 695.

(17) TPD-PF: Under nitrogen atmosphere, **7** (280 mg, 0.5 mmol), **5** (323 mg, 0.5 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (6.0 mg, 0.005 mmol), toluene (5 mL), and 2 M K<sub>2</sub>CO<sub>3</sub> (5 mL) were placed in a three-necked flask and refluxed for 72 h. After cooling, the mixture was diluted with CHCl<sub>3</sub> (20 mL) and washed with water, and the organic layer was dried over magnesium sulfate. The solvent was evaporated to 2 mL and then poured into methanol to give a precipitate. The obtained solid was redissolved in CHCl<sub>3</sub> and reprecipitated from methanol, followed by Soxhlet extraction with the same solution for 24 h to give an off-white powder (402 mg, 92%). Anal. Calcd for (C<sub>65</sub>H<sub>66</sub>N<sub>2</sub>)<sub>n</sub>: C, 89.20; H, 7.60. Found: C, 89.44; H, 7.49.  $^1\text{H}$  NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.72 (m, 2H), 7.63–7.47 (m, 8H), 7.43–7.07 (m, 20H), 6.94 (m, 2H), 2.14 (br, 4H), 1.27 (s, 2H), 0.87–0.53 (m, 28H). FT-IR (KBr),  $\nu$  (cm<sup>-1</sup>): 3060, 3033, 2958, 2925, 2871, 2857, 1594, 1492, 1466, 1322, 1275, 1180, 1099, 1027, 818, 755, 697.

**Table 1.** Molecular Weights and Thermal Properties of the Polymers

polymer	$M_w^a$	$M_w/M_n^a$	$T_d^b$ (°C)	$T_g^c$ (°C)
TPD-PFE	17 600	2.8	388	76
PFE	19 200	2.5	381	65
TPD-PF	9300	2.2	392	107

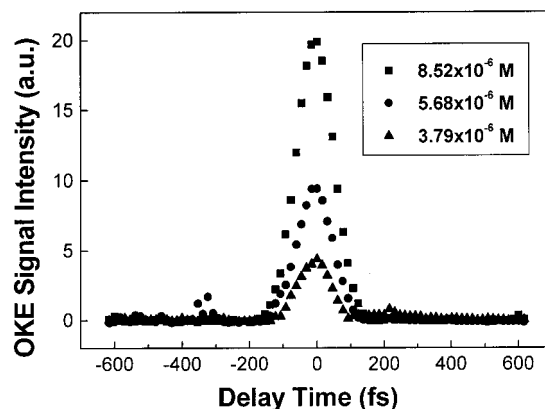
<sup>a</sup> Weight average molecular weight ( $M_w$ ) and polydispersity index ( $M_w/M_n$ ) determined by GPC in THF on the basis of polystyrene calibration. <sup>b</sup> Onset decomposition temperature measured by TGA under  $N_2$ . <sup>c</sup> Glass transition temperature measured by DSC under  $N_2$ .

**Figure 1.** Absorption spectra of TPD-PFE, PFE, and TPD-PF in  $CHCl_3$ .

TPD-PF are 388, 381, and 392 °C, respectively. The glass transition temperatures of TPD-PFE, PFE, and TPD-PF are 76, 65, and 107 °C, respectively. Thus, all of these polymers exhibit good thermal stability.

Figure 1 shows the UV–visible absorption spectra of the three polymers in  $CHCl_3$  at the same concentration of  $5.0 \times 10^{-5}$  M. The absorption peaks of TPD-PFE, TPD-PF, and PFE were observed at 393, 361, and 313 nm, respectively. The band gaps of TPD-PFE, TPD-PF, and PFE are estimated from the onset positions of the absorption bands to be 2.71, 3.00, and 2.76 eV, respectively. Compared to those of the homopolymer PFE without TPD and of the copolymer TPD-PF without alkyne, the absorption spectrum of the copolymer TPD-PFE bearing both TPD and alkyne moieties is located in the longer-wavelength region. The band gap of TPD-PFE is smaller than those of its cousins PFE and TPD-PF. Clearly, the intrachain charge transfer between the electron-deficient moiety ethynylfluorene and the electron-excessive moiety TPD exerts a bathochromic effect on the electronic transitions of TPD-PFE. In other words, the electronic structures and properties of the fluorene-based polymers can be readily tuned by molecular engineering of the co-units in the main chain.

The third-order nonlinear optical properties of these polymers in  $CHCl_3$  were measured using a femtosecond time-resolved optical Kerr effect (OKE) technique. The experimental setup, which has been described in our previous report,<sup>18</sup> used laser pulses of 830 nm with a duration of 115 fs (fwhm) and a repetition rate of 76 MHz from a Ti:sapphire laser (Coherent Mira 900F). The  $\chi^{(3)}$  value is calculated from the intensity of the OKE

**Figure 2.** Optical Kerr effect responses of TPD-PFE in  $CHCl_3$  solution at different concentrations.

signal ( $I$ ), the refractive index ( $n$ ), and the sample thickness ( $l$ ) using  $CS_2$  as a reference and was corrected for absorption using the following equation

$$\chi^{(3)} = \left( \frac{I_S}{I_R} \right)^{1/2} \left( \frac{n_S}{n_R} \right)^2 \chi_R^{(3)} \left[ \frac{\alpha l}{e^{-\alpha l/2} (1 - e^{-\alpha l})} \right] \quad (1)$$

where the subscripts S and R represent, respectively, the parameters for the sample and the reference and  $\alpha$  is the linear absorption coefficient. The last fraction comes from the sample absorption and equals 1 when the sample has no absorption around the laser wavelength used.

The OKE signals of TPD-PFE in  $CHCl_3$  at different concentrations are illustrated in Figure 2. The relatively weak background noise and contribution of the solvent have been subtracted. The nonresonant  $\chi^{(3)}$  of TPD-PFE in  $CHCl_3$  solution at a concentration of  $5.68 \times 10^{-6}$  M was deduced to be  $5.7 \times 10^{-14}$  esu by comparison with the measurements on a reference  $CS_2$  under identical conditions. The optical nonlinear response is on the same time scale as the pulse duration, and no delayed process was observed. This instantaneous response indicates that the NLO response of TPD-PFE in solution is mainly derived from the delocalized  $\pi$  electrons.<sup>19</sup>

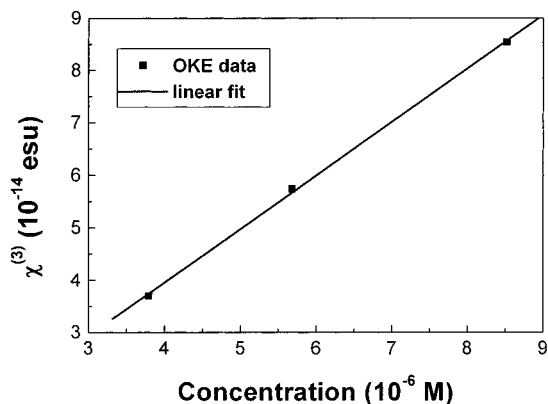
A linear dependence of the measured  $\chi^{(3)}$  on the concentration is shown in Figure 3. It is concluded that our experimental measurement is reliable, and the equation

$$\gamma = \chi^{(3)}/NL^4 \quad (2)$$

can be introduced to estimate the second-order hyperpolarizability  $\gamma$  of the sample.  $N$  is the number density of the polymer, and  $L$  is the local field factor given by  $(n^2 + 2)/3$ . Using eq 2, we calculated  $\gamma$  from  $\chi^{(3)}$  of the sample solution at a certain concentration and averaged three values as the most acceptable  $\gamma$  value for the polymer; the nonresonant  $\gamma$  value of TPD-PFE is estimated to be  $4.5 \times 10^{-30}$  esu. The measured value of  $\gamma$  for TPD-PFE can be compared with those of other conjugated polymers, particularly those of polyaryleneethylenes. Geisler et al. reported that the molecular second-order hyperpolarizability for thin films of the

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**Figure 3.** Linear fitting of the concentration dependence of  $\chi^{(3)}$  for TPD-PFE.

**Table 2. NLO Data of Three Polymers in Chloroform**

polymer	concentration (M)	$\chi^{(3)}$ (esu)	$\gamma$ (esu)
TPD-PFE	$5.68 \times 10^{-6}$	$5.7 \times 10^{-14}$	$4.5 \times 10^{-30}$
TPD-PF	$1.08 \times 10^{-5}$	$5.2 \times 10^{-14}$	$2.5 \times 10^{-30}$
PFE	$2.60 \times 10^{-5}$	$5.4 \times 10^{-15}$	$1.0 \times 10^{-31}$

thienyleneethynylene oligomers in poly(methyl methacrylate), measured by third harmonic generation (THG) using the Marker fringe technique, is  $2.3 \times 10^{-33}$  esu.<sup>20</sup> In addition, the off-resonance second-order hyperpolarizability investigated in this work compares favorably with those of many other conjugated polymers including polydiacetylenes, polyacetylenes, polyphenylenevinylenes, and polyarylenes.<sup>1</sup>

The  $\chi^{(3)}$  and  $\gamma$  data for the three polymers are summarized in Table 2. The  $\gamma$  values were found to be  $2.5 \times 10^{-30}$  esu for TPD-PF and  $1.0 \times 10^{-31}$  esu for PFE

under almost the same conditions. The value for TPD-PFE is 45 times that for its cousin without TPD and almost 2 times that for its cousin without the alkyne segment. Such enhancement is attributed to the shift of the  $\pi-\pi^*$  absorption band to longer wavelengths and the intrachain charge transfer between the electron-accepting unit ethynylfluorene and the electron-donating unit TPD in the present CT copolymer.<sup>3c</sup> One might suppose that the chosen wavelength of 830 nm could lead to a pronounced two-photon enhancement of the optical Kerr signal of TPD-PFE either if the transition to the visible  $\pi-\pi^*$  band is two-photon-allowed (e.g., because of a CT contribution) or if a one-photon-forbidden but two-photon-allowed transition is located at ca. 400 nm. However, we can argue that the two-photon enhancement of the NLO properties of TPD-PFE is negligible because our experimental results reveal that the two-photon absorption of TPD-PFE is weak.

In conclusion, a novel  $\pi$ -conjugated CT copolymer consisting of electron-donating TPD and electron-accepting ethynylfluorene and its cousins without the TPD or alkyne segments were synthesized via palladium-catalyzed coupling reactions. The ultrafast second-order hyperpolarizability of TPD-PFE was estimated to be as large as  $4.5 \times 10^{-30}$  esu in the nonresonant region, which is larger than those of its counterparts. It is truly remarkable that the NLO properties of the fluorene-based polymers can be manipulated to such a great extent (2–45 times) by simply varying the nature of the co-units in the main chain. The results lead to the conclusion that NLO properties can be enhanced strongly through the formation of an intrachain CT structure.

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