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Synthesis, Characterization, and Optoelectronic Properties of a Novel Polyfluorene/Poly(*p*-Phenylenevinylene) Copolymer

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A novel conjugated polyfluorene/poly(*p*-phenylenevinylene) copolymer containing the pendant bis(4-alkoxyphenyl) groups in the C-9 position of every alternating fluorene unit has been synthesized and well structurally characterized. The photoluminescence spectrum of this polymer exhibits strong concentration and excitation wavelength dependence in solution. The excited triplet-state maximum of polymer occurs in the region of 460−540 nm with a lifetime of 65.8 μs. This copolymer displays a minor positive nonlinear absorption at the focus of the laser irradiation, suggesting possible reverse saturable absorption. The stable electroluminescent spectrum of the polymer light-emitting diode device based on this copolymer (device configuration, indium−tin oxide/Au/copolymer/LiF/Al) was obtained with a peak wavelength of 515 nm. The bright-green emission observed over the whole active area of the copolymer closely resembles the photoluminescence of the most concentrated solution (0.5 M) used. This suggests that chain stacking in the solid state is responsible for the observed green electroluminescence.

Introduction

The ability of nonlinear optical (NLO) materials to transmit, process, and store information forms the basis of emerging optoelectronic and photonics technologies,[1] e.g., optical communications, high-speed electro-optical information processing, high-density data storage, phase conjugation, holography, spatial light modulation, short optical pulse generation, and all-optical switching as well. There are already a large number of articles concerning the design and preparation of new NLO materials over the past more than three decades; however, only a few appropriate nonlinear materials required for the practical NLO devices, including optical limiting devices, were available until now. This has been a primary barrier to the development of these optical devices.[2−4] To protect optical elements, optical sensors, and human eyes from debilitating laser effects, the intensity of incoming laser light has to be opportunely reduced.[5] An optical limiter, one of the NLO devices, which are currently of significant interest, is just such a device that strongly attenuate intense optical beams while exhibiting high transmittance for low-intensity ambient light levels. Basically, an efficient optical limiting material should have a larger ratio of the excited- to ground-state absorption cross sections ($\kappa = \sigma_{ex}/\sigma_0$), a long triplet lifetime with respect to the pulse width, and a high intersystem crossing quantum yield.[5] Many functional materials such as fullerenes,[6] carbon nanotubes,[7] polymer/nanotube composites,[8] porphyrins,[9] and phthalocyanines,[10] which exhibit high dissipative extinction nonlinearity, fast response time, large dynamic range, and broadband spectral response, have been widely studied with the view to realization of practical passive optical limiting application. Preparation of the required NLO active materials for practical optical limiters, however, still presents a significant chemical challenge.[2,3,10]

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The tunable electronic and NLO properties, low manufacturing cost, and high degree of processability of π-conjugated polymers, e.g., polythiophene, polypyrrole, polyfluorene (PFO), and poly(*p*-phenylenevinylene) (PPV) make them promising candidates as advanced materials for the development of optoelectronic applications[11] such as photovoltaic cells, biosensors, light-emitting diodes, transistors, lasers, conducting photoresists, switch elements, and data-processors in computing systems.[11,12] Of the conjugated polymers mentioned above, the polyfluorenes are attractive due to high photoluminescence and electroluminescence efficiencies and their high chemical and photochemical stability. The polymerizations of the rigid fluorene monomers, in which two phenyl rings are locked into a plane via the C-9 carbon of the fluorene units, can be realized through Stille,[13] Heck,[14] Wittig,[15] Yamamoto,[16] Grignard,[17] and Suzuki[18] coupling reactions. The facile functionalization at the C-9 position of the fluorene unit may offer an opportunity to reduce the interchain interactions thereby improving the NLO response and optoelectronic properties of the resulting polymers. Recently Chou and Shu developed a simple way to introduce 4-hydroxyphenyl functionality to the C-9 position of fluorene.[19] The main advantage of the use of an extended 9,9-bis(4-hydroxyphenyl)fluorenyl core in the polymerization reaction is that the insertion of a rigid phenylene spacer between the large side chain and the polymer backbone may lead to a more efficient shielding effect on the polyfluorene main chain, which would suppress the formation of aggregates/excimers[20] while not blocking the reaction sites of the macromonomer from the palladium-catalyzed polymerization reaction.[19] Herein, we would like to report on the synthesis and some of the photophysical and electronic properties of a novel conjugated PFO/PPV copolymer containing the pendant bis(4-alkoxyphenyl) groups in the C-9 position of every fluorene unit.

Experimental Section

General. The operations for synthesis prior to the termination reaction were carried out under purified argon. Solvents were purified, dried, and distilled under dry nitrogen. UV/vis spectra were measured on a JASCO V-530 UV/vis spectrophotometer. The ^{1}H NMR data were recorded with a LAMBDA 400 MHz spectrometer in $CDCl_3$ solvent. The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves were obtained on the Perkin-Elmer TGA-7 and DSC-7 instruments, respectively. Gel permeation chromatography (GPC) was measured on a Waters chromatography unit interfaced to a Water 410 differential refractometer using THF as the eluent and linear polystyrene as standard. The texture of the polymer was observed with a polarizing microscope (Axiolab Zeiss).

Fluorescence spectra and lifetimes were measured by a single-photon-counting method using an argon ion laser, a pumped Ti:sapphire laser (Spectra-Physics, Tsunami 3960, fwhm 150 fs) with a pulse selector (Spectra-Physics, 3980), a second-harmonic generator (Spectra-Physics, GWU-23PS), and a streakscope (Hamamatsu Photonics, C4334-01). Each sample was excited in deaerated anhydrous toluene with 410-nm laser light. Nanosecond-transient absorption measurements were carried out using third-harmonic generation (THG, 355 nm) of an Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-130, 6 ns fwhm) as an exciting source. For transient absorption spectra in the near-IR region (600−1400 nm), monitoring light from a pulsed Xe-lamp was detected with a Ge-avalanche photodiode (Hamamatsu Photonics, B2834). For the visible region (400−1000 nm), a Si−PIN photodiode (Hamamatsu Phonics, S1722-02) was employed as a detector. The picosecond transient absorption spectra were measured by the pump and probe method using a Ti:sapphire regenerative amplifier seeded by SHG of Er-doped fiber laser (Clark-MXR CPA-2001 plus, 1 kHz, fwhm 150 fs). A white continuum pulse used as a monitoring light was generated by focusing the fundamental of the amplifier on a rotating H_2O cell. The samples were excited by SHG (388 nm) of fundamental or output of OPA (Clark-MXR vis-OPA, 560 nm). The monitoring light transmitted through the sample in a rotating cell was detected with a dual MOS detector (Hamamatsu Photonics, C6140) equipped with a polychromator.

All Z-scan experiments were performed using 6-ns pulses from a Q-switched Nd:YAG laser. The beam was spatially filtered to remove the far field and tightly focused with a 9-cm focal length lens. The laser was operated at its second harmonic, 532 nm, with a pulse repetition rate of 10 Hz. All samples were prepared by dissolving the compound in a suitable common organic solvent (toluene or chloroform) at 0.5 g/L and sonically agitated until completely dissolved; homogeneous solutions were formed. All measurements were performed in quartz cells with a 1-mm path length.

Fabrication and Measurement of a Polymer Light-Emitting Diode (PLED) Device. Gold (1 nm) was evaporated (Edwards Autovac 306 Coating System) onto indium−tin oxide (ITO) at a rate of 0.2 Å/s to provide the hole-injecting contact. Polymer **4** was then spin coated from a 5 g/L chloroform solution at 900 rpm. The thickness of the film was found to be (30 ± 4) nm using atomic force microscopy (AFM, Digital Instruments, Nanoscope IIIa) to perform a step-height analysis. A thin layer (1.2 nm) of LiF was deposited at 0.1 Å/s followed by 100 nm of Al evaporated at a rate of 2 Å/s under a pressure of 3×10^{-6} mbar to form the electron injecting contact. The device area predefined by the shadow masks used is 0.06 cm^2. The devices were contacted using a test rig with gold-coated spring probes. Current−voltage data were obtained using a Keithley 2400 source-measure unit interfaced to a PC. The electroluminescence spectra were obtained using a liquid light guide coupled to an Andor 77400 Multispec spectrometer. The luminance of the polymer **4** device was measured using a calibrated Topcon BM-9 luminance meter with a Topcon AL-8 lens attachment.

Synthesis of Polymer 4. 1,4-Divinylbenzene (95%, Aldrich, 1.54 mmol), palladium(II) acetate (99.9%, Aldrich, 0.12 mmol), tri-*o*-tolylphosphine (97%, Aldrich, 0.472 mmol), tributylamine (98.5%, Aldrich, 15.95 mmol), copper(I) iodide (98%, Aldrich, 0.02 mmol), and anhydrous *N*,*N*′-dimethyl acetamide (DMAc, 10 mL) were added into a round-bottom flask containing 9,9-bis(4-hydroxyphenyl)-2,7-dibromofluorene (**2**)[19] (0.77 mmol) under highly purified

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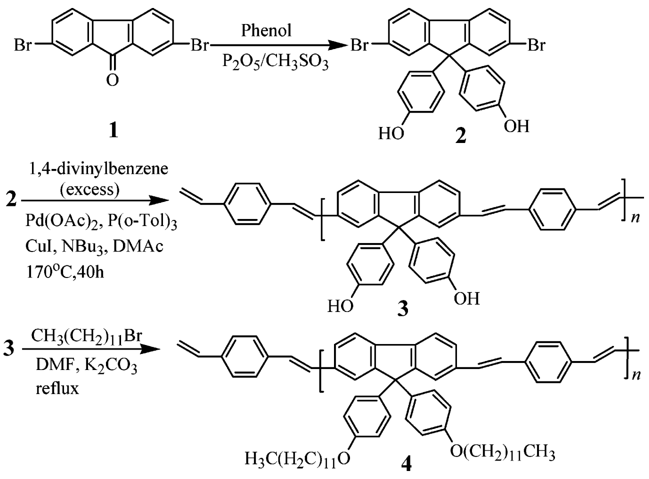
Scheme 1. Synthetic Route of Polymer 4



nitrogen. The flask was fitted with a condenser and heated at 170 °C for 40 h under static nitrogen. The reaction mixture was then poured into methanol (300 mL) with vigorous stirring. After addition, stirring continued in the absence of light for 24 h. The orange-brown precipitate was collected by filtration and transferred to a thimble, where the solids were washed by methanol for 12 h. The filtrates were then collected and dried to give a yellow solid (polymer **3**, 0. 6 g), which was further used to react with excess 1-bromododecane (98%, Aldrich, 8 mmol) in DMF (15 mL) in the presence of K_2CO_3 (98%, Aldrich, 1.25 mmol) under reflux at 110 °C for 10 h. The reaction solution was then poured into MeOH/H_2O (v/v 3/1) solution. The collected precipitate was washed with a large amount of water, dissolved in THF, and reprecipitated from methanol/water solution to give yellow polymer **4** (this procedure was repeated at least 3 times). GPC: $Mw = 4.28 \times 10^5$, $Mn = 2.2 \times 10^5$, $Pd = 1.95$. ^{1}H NMR ($CDCl_3$): δ/ppm = 0.9 ($-CH_3$), 4.0 ($-OCH_2-$), 1.3−1.8 ($-CH_2-$), 6.8−7.0 (pendant phenyl groups), 7.3 ($-CH{=}CH-$), 7.5−7.7(aromatic protons of fluorene and phenylene units in the polymer backbone). UV/vis (in benzonitrile: λ_{max}/nm = 427, 450 (shoulder). Photoluminescence (in benzonitrile; 2.6×10^{-4} mM): $\lambda_{max}{}^{fluo}$/nm = 474, 500 (shoulder). τ_f = 584 ps (88%), 1.38 ns (12%).

Results and Discussion

As shown in Scheme 1, the acid-catalyzed condensation reaction of 2,7-dibromo-9-fluorenone (**1**) with excess phenol gives 9,9-bis(4-hydroxyphenyl)-2,7-dibromofluorene (**2**),[19] which was directly used to copolymerize with 1,4-divinylbenzene (95%, Aldrich) through a typical Heck-coupling reaction to produce polymer **3**. It should be noted that synthesis employs a 2-fold excess of 1,4-divinylbenzene in order to remove any residual bromine functionalities, which might act as fluorescence quenching sites. The two alkoxyl side chains in the resulting light-yellow polymer **4** are added by reacting the 4-hydroxyphenyl groups of **3** with excess 1-bromododecane in the presence of potassium carbonate. This polymer is highly soluble in many common organic solvents, e.g., THF, chloroform, benzonitrile, and others, but is less soluble in toluene. The ^{1}H NMR spectrum of **4** in $CDCl_3$ is consistent with the expected structure of the alternating PFO/PPV copolymer (see Experimental Section).

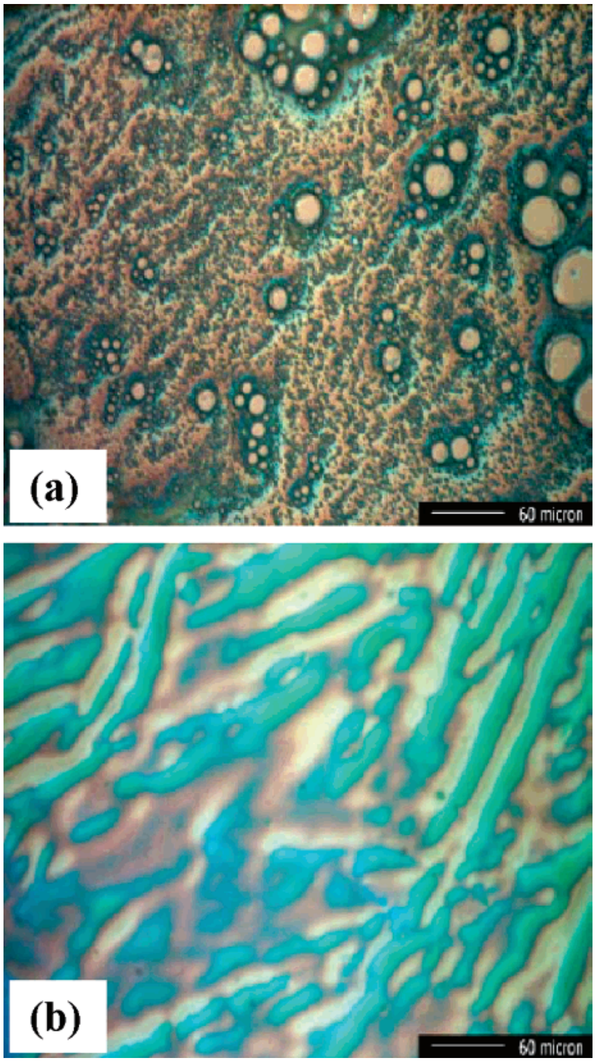


Figure 1. Polarized optical images of Polymer **4** (a) at room temperature and (b) after heating at 100 °C for several minutes.

The thermal properties of the resultant polymer **4** were studied by TGA, DSC, and polarized optical microscopy (POM). As shown in Figure 1, on heating, the solid crystalline phase at room temperature is transformed into a viscous birefringent liquid with a typical liquid-crystalline pattern, suggesting the formation of the ordered structure. The glass-transition temperature (T_g) of polymer **4** is about 95 °C, which is higher than those of poly(9,9-dioctylfluorene) (∼51 °C)[21] and poly(9,9-dihexylfluorene) (∼55 °C)[22] due to the attachment of two 4-dodecyloxyphenyl groups onto the C-9 position of every fluorene unit. The TGA thermogram of **4** exhibits two weight-loss plateaus. At lower temperatures, almost no weight loss was observed. The 4-dodecyloxy side chain in copolymer decomposed first at 160−320 °C; its onset temperature for the thermal bond cleavage is at 210 °C. Then the polymer backbone was subjected to decomposition at 350−500 °C, where the onset temperature for the thermal bond cleavage is at 404 °C. These findings indicated that the resultant polymer has good thermal stability.

The UV/vis absorption spectra of **4** in dilute benzonitrile (BN) solution and in thin film are shown in Figure 2. The

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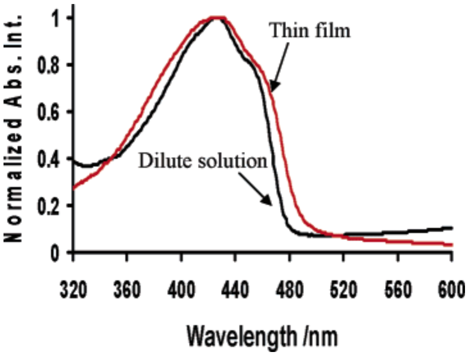

Figure 2. UV/vis absorption spectra of polymer **4** in the dilute benzonitrile solution (2.6 × 10^{-4} mM) and in the thin film.

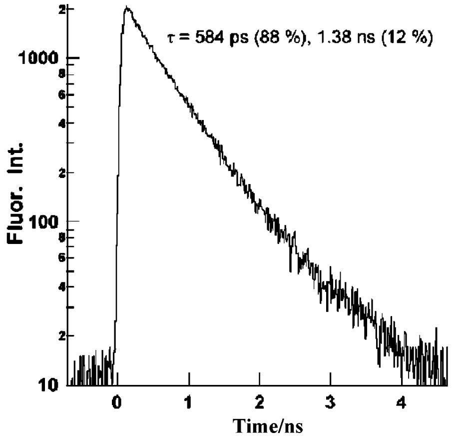

Figure 3. Fluorescence decay of polymer **4** in benzonitrile (0.14 mM) at 474 nm (λ_{ex} = 410 nm).

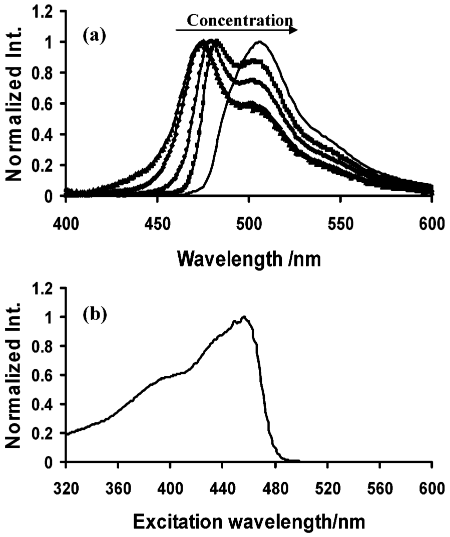

Figure 4. (a) Concentration dependence of PL spectra of polymer **4** in benzonitrile solution excited at a wavelength of 410 nm, from left to right: 2.1 × 10^{-6}; 2.6 × 10^{-4}; 8.7 × 10^{-3}; 2.6 × 10^{-2}; 0.5 M. (b) Excitation spectrum of polymer **4** in benzonitrile (0.026 mM).

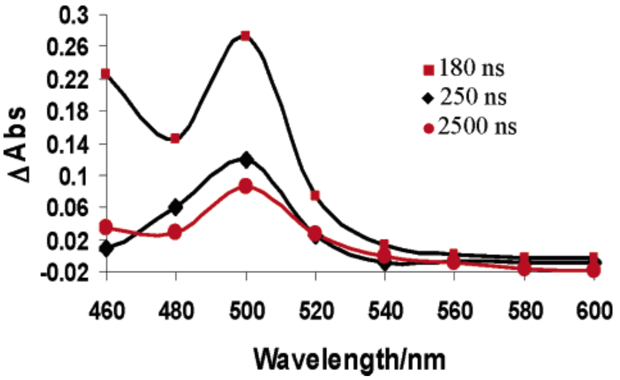

Figure 5. Nanosecond transient absorption spectra of polymer **4** (0.14 mM) in deoxygenated benzonitrile at different time. The excitation consisted of nanosecond irradiation at 355 nm.

main absorption peak in the UV/vis spectrum of **4** is located at 427 nm, followed by a shoulder peak at 450 nm. They are attributed to the $\pi-\pi^*$ transition of the polymer. By comparison of the thin film and dilute solution UV/vis spectra of **4**, it can be clearly seen that the absorption spectrum of the thin film is apparently broader, but the positions of the main absorption peaks are almost unchanged. As expected, the polymer **4** exhibits very strong photoluminescence (PL) with maximum emission peaks centered at 474 nm in dilute benzonitrile solution (see Supporting Information). The fluorescence of the thin-film spin coated onto an ITO-coated glass substrate was almost completely quenched due to possible energy transfer to ITO, but the emission peak at around 500 nm in the PL spectrum of **4** is still clearly resolved. Similar observation on the quenching of PL of PPV spin coated onto ITO was reported by Herold et al.[23] The quenching of PL means in general that the electroluminescence (EL) efficiency is quenched, too.[23] To overcome this problem, an alternative method is to use fluorine-doped tin dioxide (FTO)[23] or modified ITO instead of ITO substrate. The fluorescence decay monitored at 474 nm (λ_{exc} = 410 nm) in deoxygenated dry benonitrile shows two exponential-decay processes (Figure 3). From the initial fast decay part of **4**, lifetime (τ_{f1}) of the single excited state is 584 ps (fraction of this component, 88%). From the slow decay part of **4**, the lifetime (τ_{f2}) of another singlet excited state is 1.38 ns (fraction of this component, 12%). The value of the latter is quite close to the fluorescence lifetime of typical PPV polymer (about 1.27 ns). Furthermore, the concentration and excitation-wavelength dependence of the PL spectra of polymer **4** are apparently observed in benzonitrile solution, as shown in Figure 4. The maximum PL peak is shifted gradually to the longer wavelengths with the increase of the polymer concentration from 2.1 × 10^{-6} to 0.5 M (in repeat units), suggesting the formation of aggregates (leading to excimers) in solution. The intensity of the emission band is apparently enhanced in the red wavelengths due probably to the addition of the interchain to the intrachain exciton recombination.[24] When the concentration is kept unchanged (0.026 mM in benzonitrile) but the excitation wavelength is changed from 320 to 500 nm, the PL intensity of polymer **4** reached a maximum at λ_{ex} = 456 nm, which is close to the red edge of the main absorption band.

The nanosecond transient absorption spectrum was obtained by the excitation of the polymer **4** with 355-nm laser light in deaerated benzonitrile, as shown in Figure 5, in which the rapid and slow components of the decay were observed; both components showed the same absorption band at 500

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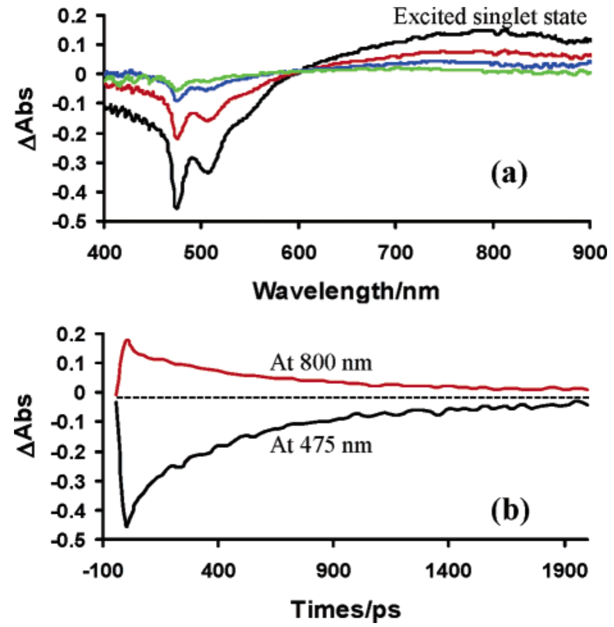

Figure 6. (a) Picosecond transient absorption spectra of polymer **4** in benzonitrile (0.5 mM) at different times. From bottom to top: 40 (black curve), 400 (red curve), 1000 (blue curve), and 2000 (green curve) ps. (b) Absorption−time profiles of **4** in benzonitrile (0.5mM) at 475 (black curve) and 800 nm (red curve), respectively.

nm. On addition of O_2, the transient absorption band showing slow decay at 500 nm, which is attributed to triplet−triplet (T−T) absorption in this polymer, vanished, suggesting that the energy transfer takes place from the triplet excited states of **4** to O_2, probably yielding ${}^1O_2$. In the absence of O_2, the slow decay rates depend on the laser powers, suggesting the intermolecular T−T annihilation is due to the collision between the highly concentrated triplet states.

$$2\,{}^3\text{polymer }\mathbf{4}^* \xrightarrow{k_{TT}} \text{ploymer }\mathbf{4} + {}^1\text{polymer }\mathbf{4}^* \qquad (1)$$

The rate constants of first- and second-order kinetics were separately evaluated using the following equation

$$-\mathrm{d}[\ln(\Delta A_0)]/\mathrm{d}t = \Delta k_{1st} = k_T{}^0 + (2k_{TT}/\epsilon_T)\Delta A_0 \qquad (2)$$

where ΔA_0, $k_T{}^0$, and ϵ_T are T−T absorbance at $t = 0$, intrinsic first-order decay rate of the triplet excited state of polymer **4**, and extinction coefficient of the triplet absorption band, respectively. The plot of Δk_{first} to ΔA_0 shows a linear correlation (see Supporting Information). The intercept gives the value $k_T{}^0$, from which the lifetime of the triplet state ($\tau_T = 1/k_T{}^0$) was calculated to be 65.8 μs, which is much longer than the laser pulse duration (ca. 6 ns) of the nanosecond laser system used for photophyscial measurements. It is interesting to note that the triplet-state maximum of **4** occurs in the region of 460−540 nm, which is just located in the high-transmittance region in the UV/vis absorption spectrum of the sample (Figure 2). This implies that this region is of particular interest for reverse saturable absorption based optical limiting since it ensures that the absorption cross section of the excited state always exceeds the ground-state absorption cross section.[25] Figure 6 gives the picosecond transient absorption spectra and time profiles of polymer **4** in benzonitrile solution. It can be seen that the excited singlet-state absorption maximum appears at around 800 nm; its decay is followed by the recovery of the emission at 470 nm. The singlet lifetime calculated from the picosecond decay shown in Figure 6b is about 591 ps, which is quite close to the fluorescence lifetime of the first component (τ_{f1} = 584 ps) previously mentioned.

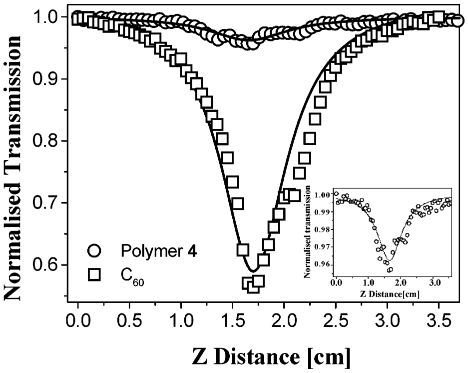

Figure 7. Open aperture z-scan spectra of C_{60} and polymer **4** at 532 nm with normalized transmission plotted as a function of sample position in the *z* direction. The incident laser intensity was calculated as 0.4 GW cm^{-2} for both materials. Inset: Magnified open-aperture z-scan spectrum for polymer **4**, displaying positive nonlinear absorption.

The open-aperture z scans performed in this study in all cases exhibited a reduction in the transmission about the focus of the lens. This was typical of an induced positive nonlinear absorption of the incident light, in this case assumed to be due to reverse saturable excited-state absorption. Hercher[26] conducted a general analysis of saturable absorbers using a three-level scheme. This theoretical analysis of excited-state absorbing materials and optical limiting was further adapted and advanced.[27−30] Nonlinear optical coefficients were calculated for $C_{60,}$ an established optical limiting absorber,[31,32] in order to compare the resulting NLO properties of polymer **4**. Upon initial analysis of the data from the z-scan experiment, the copolymer displayed a minor positive nonlinear absorption at the focus of the laser irradiation, suggesting possible reverse saturable absorption. This resultant NLO effect was however noticeably less than that displayed by the C_{60} sample as illustrated in Figure 7. A low linear absorption coefficient (α_0) at 532 nm, of 0.58 cm^{-1} for polymer **4** (compared with 2.72 cm^{-1} for C_{60}), was also calculated, suggestive of a low absorption response. The nonlinear absorption noted for the two materials differs only slightly with polymer **4** exhibiting a lower value of (2.1 ± 0.4) × 10^{-9} cm W^{-1} when compared to β_I of (4.7 ± 0.9) × 10^{-8} cm W^{-1} for the C_{60}. The absorption cross-section ratios ($\kappa = \sigma_{ex}/\sigma_0$) of C_{60} and polymer **4** are found to be 5.2 ± 0.6 for C_{60} and 2.86 ± 0.4, respectively.

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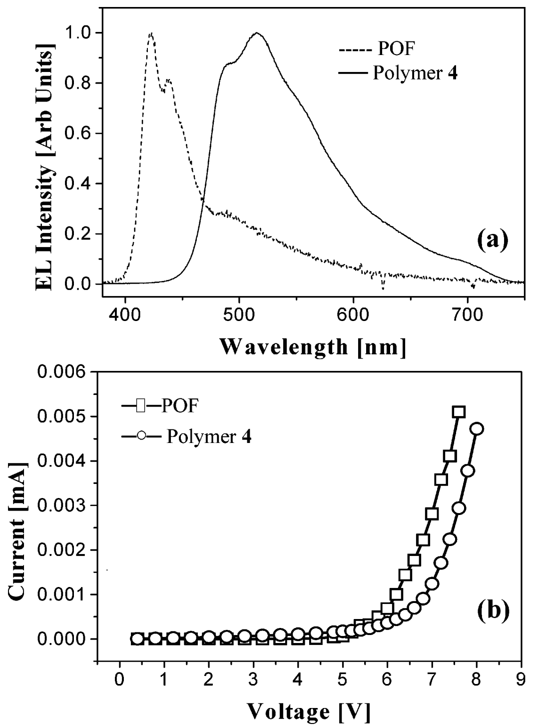

Figure 8. (a) EL spectrum obtained for polymer **4**, including the EL spectrum for POF material for comparison. (b) Current−voltage characteristics for the polymer **4** device and an identical device substituting in POF in place of the copolymer.

This novel copolymer was also used as the emissive layer in a PLED, which was tested in air at room temperature. The sandwich-type structure used was ITO/Au/polymer **4**/LiF/Al. The polymer, poly(9,9-di-*n*-octylfluorenyl-2−7′-diyl) (POF, obtained from the American Dye Source, Inc., product code ADS129BE), a very promising blue light-emitting material with high quantum yield either in solution or in the solid state, was used as a reference material only for the electroluminescent experiments as it displays no intensity-dependent optical response at 532 nm.[33] The stable EL spectrum of polymer **4** obtained is shown in Figure 8a with a peak wavelength of 515 nm, along with that from a similar device made with POF, which had a peak emission at 422 nm. From the PL data in Figure 4, it is clear that the bright-green emission observed over the whole active area of the PLED of polymer **4** closely resembles the PL of the most concentrated solution (0.5 M) used. This suggests that chain stacking in the solid state is responsible for the observed green EL. Figure 8b shows the current−voltage characteristics of the devices fabricated with polymer **4** and PFO. The curves are very similar with the POF having a slightly lower operating voltage of 6.2 V compared with 6.8 V for polymer **4** at a current density of 167 Am^{-2}, which suggests that there is better hole injection in the POF device. The peak brightness at 10 mA was just 8.6 $\mathrm{cd/m}^2$, which corresponds to an external efficiency of 0.012%. Because of the small amount of polymer **4** available, the emissive layer had to be spin coated at low rpm from a dilute solution in order to get a uniform thin film. The resulting emissive layer was measured to be 30 nm thick using AFM. Typically a more concentrated solution (e.g., 15 mg/L) and a higher spin speed (e.g., 1500 rpm) would result in an emissive layer thickness between 100 and 150 nm. The thinness of the emissive layer combined with the fact that the polymer **4** device was a single-layer device contributed to the low efficiency of this particular device.

Conclusion

A novel conjugated PFO/PPV copolymer containing the pendant bis(4-alkoxyphenyl) groups in the C-9 position of every fluorene unit was prepared. This polymer is highly soluble in many common organic solvents, e.g., THF, $\mathrm{CHCl_3}$, benzonitrile, and others. The polymer exhibits very strong PL with maximum emission peaks centered at 474 nm in dilute benzonitrle and a single glass-transition temperature at about 95 °C. The fluorescence of the thin film spin coated onto the ITO substrate was almost completely quenched. The main absorption peak in the UV/vis spectrum of polymer **4** is located at 427 nm, followed by a shoulder peak at 450 nm. The excited triplet-state maximum of polymer **4** occurs in the region of 460−540 nm with a lifetime of 65.8 μs. Upon initial analysis of the data from the z-scan experiment, the copolymer displayed a minor positive nonlinear absorption at the focus of the laser irradiation, suggesting possible reverse saturable absorption. This resultant NLO effect was, however, noticeably less than that displayed by the $\mathrm{C_{60}}$ sample, indicating a relatively low efficiency of energy transfer between excited singlet and triplet states with this polymer. The stable electroluminescent spectrum of the PLED device with configuration of ITO/Au/polymer **4**/LiF/Al was obtained with a peak wavelength of 515 nm. The stacking of the polymer chains in the solid state is responsible for the observed green electroluminescence. Although preliminary tests yielded relatively low performance devices, future devices using an optimized multilayer structure are expected to result in much higher external quantum efficiencies.

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Supporting Information Available: PL spectra, absorption-time profiles, and thermogravimetric curves of polymer 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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