

High luminescent efficiency in light-emitting polymers due to effective exciton confinement

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Highly efficient light-emitting polymers have become possible by molecular engineering. Photoluminescence (PL) quantum yield above 90% in the solid state is reported for the alternating block copolymer of distyrylbenzene. We conclude that the alternate arrangement of conjugated and nonconjugated segments with surrounding side groups for chromophores effectively confine the excitons for radiative emission. The effectiveness of the exciton confinement is confirmed through the temperature independence of the PL quantum yield. The time-resolved PL decay measurement supports this model through the independence of the PL yield on temperature and emission wavelength. The synthesized copolymers have been employed for the fabrication of electroluminescent (EL) devices, demonstrating high external EL efficiency with low operation threshold. © 2000 American Institute of Physics. [S0003-6951(00)03405-7]

The commercial potential of polymer light-emitting diodes (PLEDs) has stimulated much work on the improvement of polymer functions,¹ optimization of device structures,²⁻⁵ and understanding of the photophysics.⁶⁻⁸ Polymers containing chromophores of phenylene vinylene (PV) are well-studied light-emitting polymers commonly used for the PLED fabrication.⁹ However, the relatively low photoluminescence (PL) quantum efficiency (~25%) of poly(*p*-phenylene vinylene) (PPV)¹⁰ motivates further consideration of molecular engineering that can be used to improve the optical and electric properties as well as other properties, such as the processibility of the polymers.

One approach to attaining high PL efficiency and solubility is to design alternating rigid conjugated segments and flexible nonconjugated segments along the polymer backbone.¹¹ The interruption of the π conjugation will effectively confine the exciton within the conjugated segments, while the inserted flexible segments can improve the solubility of the polymer. These ideas have been employed to guide synthesis of PPV-related alternating block copolymers,^{11,12} successfully demonstrating high performance of the electroluminescent (EL) and lasing devices based on the copolymers.¹¹⁻¹⁵ The EL quantum efficiency of PPV-related alternating block copolymer is much higher than the reference PPV.

To characterize further the effect of exciton confinement in PPV-related alternating block copolymers, in this letter we report the measurement of absolute PL quantum efficiencies and investigate the effectiveness of the exciton confinement of the design of the alternating block copolymer with substi-

tution of side chains on both sides of each phenylene ring. By attaching methoxy side groups to different positions of the benzene rings, the interchain interaction can be further reduced to enhance the exciton confinement, in which the side groups act more or less similarly to a dilution effect for PV chromophores. As a result, the highest PL efficiencies achieved by us is 96%, one of the highest PL efficiencies ever reported for the solid state.

While fluorescent oligomers usually show high PL efficiency in dilute solution, for example, 90% for 1-4-distyrylbenzene in the blue region,¹⁶ they generally have low PL efficiency in the solid phase (<10%). The factors affecting the PL yield in the solid state are mainly intermolecular coupling of emitting states (through formation of aggregates), the twisting of the molecular units (nonplanarity), and migration of excitation energy to distortions and impurity traps. By starting from the distyrylbenzene monomer which is an oligophenylenevinylene (2 1/2 PV), efficient alternating block copolymers were synthesized for blue light emission.¹¹ We have synthesized a series of green distyrylbenzene block copolymers (GDBBCs) by attaching methoxy side groups to 2 1/2 PV. The attached methoxy side groups, not only red-shift the emission color to green, but also increase interchain distance, thereby decreasing interactions in the solid state. In this letter, we will mainly focus our attention on the determination of the properties of the GDBBC, poly [1,6-hexanedioxy-2,6-dimethoxy-1,4-phenylene]-1,2-ethenylene-[3,6-dimethoxy-1,4-phenylene]-1,2-ethenylene-[3,5-dimethoxy-1,4-phenylene], in which each phenylene ring has two methoxy substituents. With this configuration, the conjugated segments in the main chain can be effectively shielded from interchain interactions.

The GDBBC forms a green powder, has an average mo-

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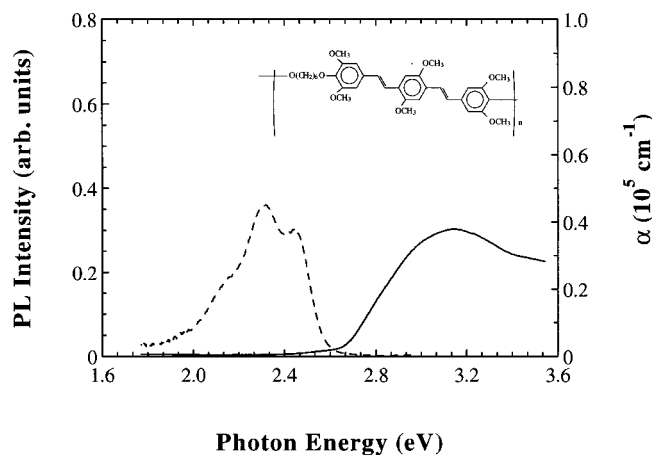


FIG. 1. Chemical structure of the GDBBC and optical absorption and PL spectra of the GDBBC solid thin film.

molecular weight (\bar{M}_w) of 1.5×10^4 (GPC), dispersity of 2.05, and contains 40 chromophores in an average molecular chain. It is easily dissolved in common solvents such as toluene and chloroform and can be spin coated into thin films of good quality using a concentration 10 mg/ml of sample polymer solution. The PL and absorption spectra were measured using a PTI Quantmaster and a Perkin-Elmer Lambda spectrometer, respectively. The PL quantum efficiency was measured using an integrating sphere (Newport 819-IS-4); the excitation light from a 100 W xenon lamp was detected through a monochromator with a photodiode (UDT-UV100). The surface reflection of the integrating sphere and the quantum efficiency of the photodiode were provided by the manufacturers. The cyclic voltamogram was recorded in 1 M hydrochloride aqueous electrolyte using a Pt working electrode and a saturated calomel electrode reference electrode. The time-resolved PL was measured by the time correlated single photon counting technique. The excitation light was from a synchronously pumped dye laser (stilbene) at 3.02 eV (less than 50 mW/cm^2 on the sample) with ~ 5 ps pulse width. The instrument response function from this system is ~ 40 ps, providing access to lifetime components as short as ~ 10 ps through curve fitting methods. The samples were measured by a profilometer (Alpha-Step 500) to be 100–300 nm thin films on quartz substrates. The sheet resistance of the indium-tin-oxide (ITO) used is $\sim 20 \Omega/\text{square}$. The metal electrode of the EL device was prepared by vacuum deposition at 1×10^{-7} Torr. The EL intensity was measured by a calibrated photodiode.

The optical absorption spectrum of the GDBBC thin film in Fig. 1 shows a structureless broad absorption band from 2.67 to 3.35 eV, which resembles those of alkoxy-substituted 2 1/2 PV oligomers.^{16,17} The maximum absorption coefficient is $3.8 \times 10^4 \text{ cm}^{-1}$ at 3.17 eV. The energy gap (taken as the absorption edge) of the GDBBC is 2.6 eV. From the cyclic voltamogram, the ionization potential of the GDBBC is 5.6 eV. The electron affinity energy of 3.0 eV is calculated by subtracting the ionization potential from its energy gap.

The GDBBC excited at 3.1 eV (Fig. 1), shows a green emission consisting of peaks at 2.45, 2.31, and 2.17 eV, with vibronic structure typical of PPVs and PPV oligomers. The absolute PL efficiency was measured by the methods described in Ref. 10. The PL efficiency η is defined as

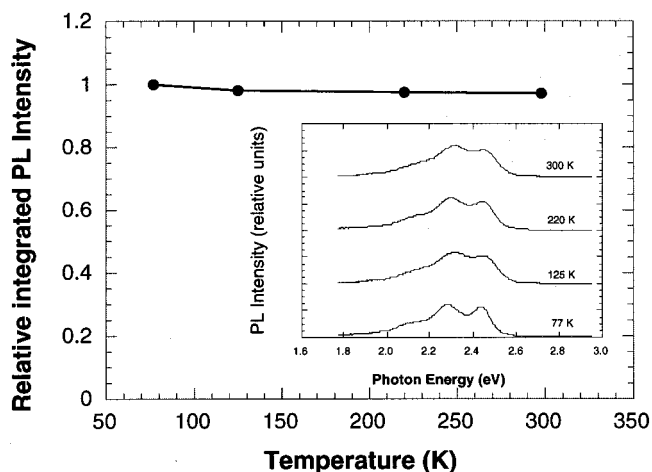


FIG. 2. Temperature dependence of integrated PL intensity of the GDBBC. (Inset) Photoluminescence spectra of the GDBBC at different temperatures.

$$\eta = X/Y, \quad (1)$$

where $X = [I_{\text{sample}} - (1-A)I_{\text{sphere}}]/AI_{\text{ex}}$, and Y is a calibration factor determined by system parameters.¹⁰ Here I_{sample} is the PL intensity of the sample; I_{sphere} is the intensity of the sample with nondirect sample illumination, A is absorbance, and I_{ex} is the intensity of excitation light. We measured the quantum efficiencies for a series of GDBBC samples

$$\eta = 90\text{--}96\%.$$

Generally, there are a number of factors such as impurities, structural order, and temperature that may affect the PL quantum efficiencies. To demonstrate the effectiveness of exciton confinement in our samples, we measured the temperature dependence of the PL of the GDBBC from 77 to 300 K. When the temperature was decreased to 77 K, the vibrational features narrowed slightly, however, the integrated intensity of the spectrum did not change significantly as compared with that at room temperature (Fig. 2). Thus the thermal deactivation of excitons is effectively limited, due to the alternating block design with surrounding side groups.

To verify the effectiveness of exciton confinement, we also studied the time-resolved PL decays of the GDBBC. The PL decays of the GDBBC at different emission wavelengths and different temperatures are shown in Figs. 3(a) and 3(b). The results are insensitive to the emission wavelengths and temperature. In all the cases for $t < 3$ ns shown in Figs. 3(a) and 3(b), the decay of the PL is approximately single exponential, i.e.,

$$I = I_0 \exp(-t/\tau), \quad (2)$$

with a time constant of $\tau = 1.24 \pm 0.05$ ns, reflecting no obvious nonradiative decay channels. For $t > 3$ ns a small slower decay component becomes apparent. This component is also emission wavelength and temperature independent, demonstrating that it is not due to (temperature dependent) exciton migration to aggregated segments (with subsequent slower emission) or energy transfer from high energy excited states to low energy excited states. We suggest that the nonconjugated segments and the methoxy groups have effectively confined the excitons to single chromophores; this slower component is likely due to small variation in the chro-

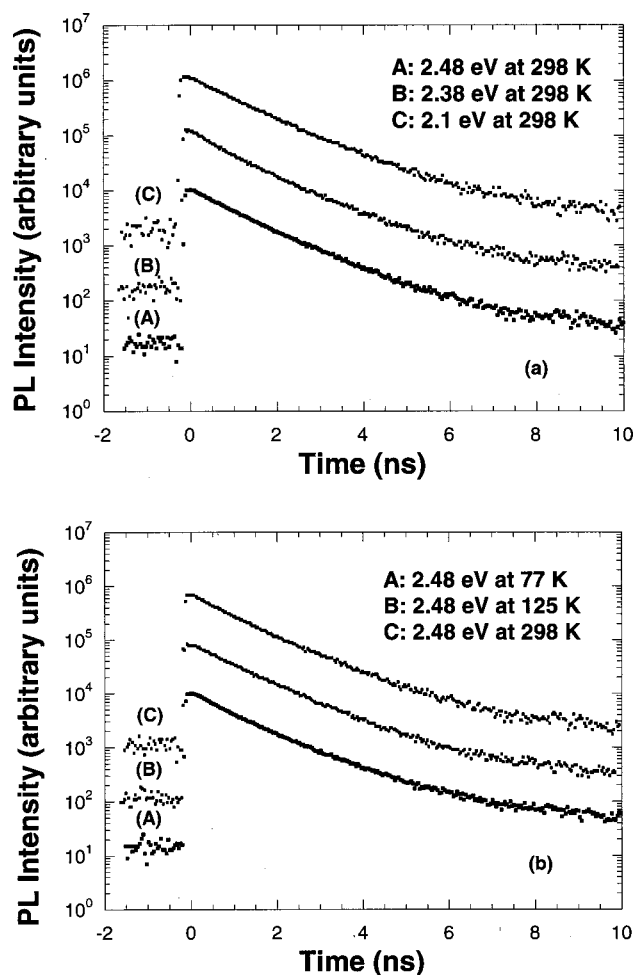


FIG. 3. PL decay of the GDBBC (a) at different emission bands at 298 K: (A) 2.48 eV; (B) 2.38 eV; and (C) 2.1 eV. (b) At different temperatures for emission at 2.48 eV: (A) 77 K; (B) 125 K; and (C) 298 K.

mophore environment. The dominant τ of 1.24 ns is short, supporting the importance of exciton confinement in achieving high efficiency.

As compared to the previous GDBBC reported in Ref. 15, the GDBBC with two methoxy substituents attached to all the phenylene rings is 10%–20% higher in PL efficiency. This shows that the larger number of surrounding methoxy side groups further shields the PV chromophores from interchain interactions.

GDBBCs with high PL efficiency are expected to be used in LED fabrication. To this end, electroluminescent devices were constructed using the GDBBC as the light-emitting layer. In order to facilitate the hole transport, a layer of hole-transporting poly[1-phenyl-2-(*p*-*n*-carbazolylphenyl)acetylene] (PDPA-Cz),¹⁸ which has a 5.3 eV ionization potential, is also inserted to bridge ITO (4.8 eV) and the GDBBC (5.6 eV). We employed 8-hydroxyquinoline aluminum as an electron injection layer to fabricate a structure of ITO/PDPA-Cz (40 nm)/GDBBC (40 nm)/Alq (35 nm)/MgAg. The threshold of electroluminescent emission for the device was 2.5 V, and the brightness reached 1650 cd/m² at 7 V operated in air. The luminance–voltage (L – V) and current–voltage (J – V) characteristics are shown in Fig. 4. The external EL quantum efficiency is \sim 1%.

In conclusion, the distyrylbenzene alternate block copolymers designed with side groups surrounding chro-

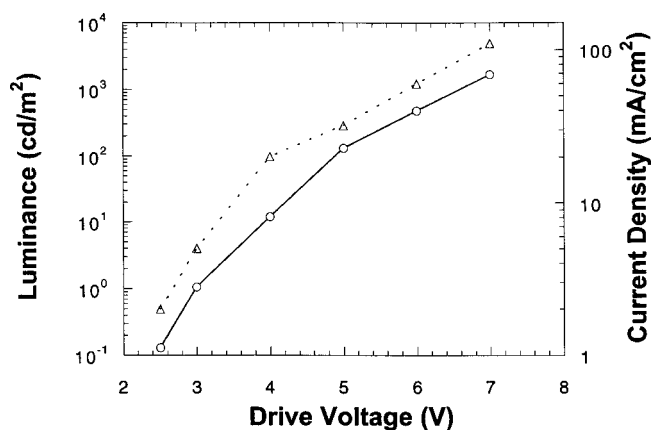


FIG. 4. The luminance–voltage (L – V) (circles) and current–voltage (J – V) (triangles) curves of an ITO/PDPA-Cz/GDBBC/Alq/MgAg device.

mophores were synthesized. These PL quantum yields approach unity. The high PL quantum efficiency of the designed polymers is attributed to the confinement effects of the nonconjugated segments and the moieties around the chromophores, which together act as confinement cages, effectively preventing the diffusion of the excitons and decreasing the interchain interactions. With a heterostructure of ITO/PDPA-Cz/GDBBC/Alq/MgAg, we have shown an efficient green triple-layer LED (1% of external EL efficiency) with a low threshold voltage (2.5 V).

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