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Semiconducting Polymer Quantum Wires

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Abstract

Semiconducting polymer heterostructures with strong two-dimensional quantum confinement of excitons are prepared by self-assembly of two conjugated polymers in binary blends. Exciton confinement effects in the semiconducting polymer quantum wires were observed at room temperature by photoluminescence excitation and photoluminescence spectroscopies and by electric field-induced photoluminescence quenching. Observation of new exciton states, enhanced luminescence, and stability of luminescence at high electric fields (3×10^6 V/cm) confirmed the one-dimensionality of the excitons in the organic quantum wires.

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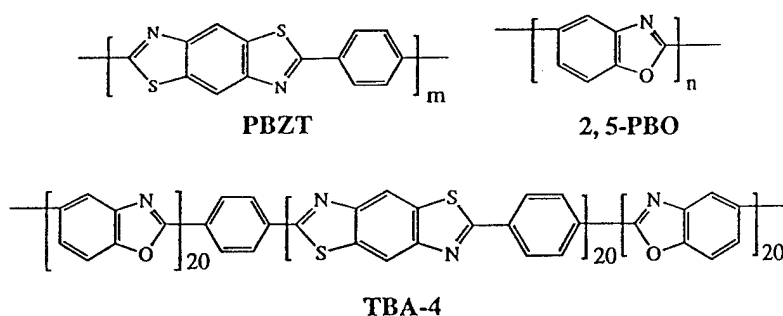
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Semiconducting polymers are currently being explored in various solid state electronic and optoelectronic devices, including thin film transistors, light emitting diodes, photovoltaic cells, photodetectors, xerographic photoreceptors, and lasers.¹⁻⁵ Low dimensional organic semiconductors⁶⁻¹² such as *quantum wires*, *quantum boxes*, and *superlattices* are expected to exhibit enhanced or novel electronic and optical properties that could significantly improve such devices in ways analogous to low dimensional inorganic semiconductors.^{13, 14} Because of their linear chain structures and the dominant role of electronic delocalization along the chain on their electronic and optical properties, π -conjugated or semiconducting polymers have generally been thought to be quasi one-dimensional (1-D) materials or "natural quantum wires".¹ However, recent advances in understanding of solid state semiconducting polymers suggest that they are best regarded as three-dimensional (3-D) bulk materials due to chain aggregation and strong interchain interactions.^{4, 15} We believe that the failure of all prior attempts^{9, 10} to prepare quantum confined heterostructures of semiconducting polymers and to observe the predicted quantum confinement effects is in part due to interchain interactions and chain aggregation which result in structures that are orders of magnitude larger than the exciton Bohr radii of the materials.^{11, 16} In contrast, all the theoretical calculations which predict quantum confinement effects in heterostructured semiconducting polymers have been made on *isolated single polymer chains*.^{7, 8}

We recently reported a new and general self-assembly approach to preparing semiconducting polymer quantum boxes and the first observation of the discrete exciton energy levels in a quantum confined organic semiconductor.¹² In this approach, self-organization of binary blends of a triblock conjugated copolymer with one of its parent homopolymers creates semiconducting polymer heterostructures in which 3-D confined boxes with monomolecular sizes are well defined. Here, we

use this approach to prepare semiconducting polymer *quantum wires* and demonstrate quantum confinement effects on the 1-D excitons.

The semiconducting polymer quantum wires were prepared from the triblock conjugated copolymer poly(2,5-benzoxazole)-*block*-poly(p-phenylene benzobisthiazole)-*block*-poly(2,5-benzoxazole) (TBA-4) and the homopolymers poly(p-phenylene benzobisthiazole) (PBZT) and poly(2,5-benzoxazole) (2,5-PBO) whose structures are shown below:



The synthesis and characterization of these polymers have been described elsewhere.^{11, 17} The parent homopolymers PBZT and 2,5-PBO of the triblock copolymer TBA-4 have energy band gaps, based on optical absorption edges, of 2.48 and 3.24 eV, respectively. Each triblock copolymer chain thus contains a single quantum well with a potential barrier of $\Delta E_g = E_g^A - E_g^B = 0.76$ eV. To achieve lateral confinement and complete isolation of the triblock chains, we prepared binary blends of TBA-4 with 2,5-PBO. From the known X-ray diffraction data for PBZT and 2,5-PBO homopolymers, the cross-sectional area of a PBZT chain is $(0.35 \times 0.58 = 0.203)$ nm² and the repeat unit lengths of PBZT and 2,5-PBO are 1.25 and 1.16 nm, respectively.^{11, 18} The average length of each PBZT segment in TBA-4 is 20 repeat units or 25 nm. Compared to the exciton Bohr radius of bulk PBZT ($a_B = 13$ Å),¹⁶ these sizes suggest that isolated chains of TBA-4 in 2,5-PBO matrix represent PBZT quantum wires with strong 2-D lateral confinement and no confinement along the chain. The TBA-

4/2,5-PBO blend composition is specified in terms of mole % PBZT repeat units; thus, 2 and 0.5% blends contain 1 TBA-4 chain per 16 and 66 chains of 2,5-PBO, respectively.

Thin films of TBA-4/2,5-PBO blends on silica or indium-tin-oxide (ITO) substrates were prepared by spin coating of their solutions in trifluoroacetic acid, washing in triethylamine solutions, and vacuum drying at 60°C. The film thickness of all samples was typically in the range of 100-180 nm and was measured by using a Tencor Northern Alpha Step profilometer. Optical absorption spectra were obtained with a Perkin-Elmer Model Lambda 9 UV-Vis-near IR spectrophotometer. Steady state photoluminescence (PL) and photoluminescence excitation (PLE) studies were done on a Spex Fluorolog-2 spectrofluorometer equipped with a Spex DM3000f spectroscopy computer. The thin film samples for PL or PLE studies were positioned such that the emission was detected at 22.5° from the incident radiation beam. Relative PL quantum efficiencies were obtained by integration of PL emission spectra. Further details of all photophysical measurement techniques can be found in our previous reports.^{3,4,15} Aluminum electrode was evaporated onto thin film samples on ITO glass for electric field-induced PL quenching experiments; a positive bias voltage was applied while the sample was photoexcited and the emission collected.

The room temperature (298K) optical absorption spectra of thin films of pure TBA-4 and TBA-4/2,5-PBO blends showed only absorption bands characteristic of the PBZT and 2,5-PBO homopolymers. The absorption spectrum of pure TBA-4 shown in Fig. 1 clearly reveals bands due to PBZT with maxima at 440 nm (2.82 eV) and 470 nm (2.64 eV) and 2,5-PBO with a maximum at 360 nm (3.44 eV) and a shoulder at 344 nm (3.60 eV). Only these absorption bands were also found in the spectra of the TBA-4/2,5-PBO blends. This result means that there is spatial confinement of excitons in the two energetically different segments of the triblock copolymer chains.

Such an electronic localization phenomenon in block conjugated copolymer chains is essential but is not sufficient evidence that the PBZT block of an isolated TBA-4 chain in the 2,5-PBO matrix is a *quantum wire*.

The PLE spectrum of TBA-4 thin film (monitored at 600 nm) was found to be similar to its optical absorption spectrum (Fig. 1). In contrast, the PLE spectra of TBA-4/2,5-PBO blends shown in Fig. 1 are dramatically different from the corresponding optical absorption spectra in that new peaks are observed in the PLE spectra. The intensity of the new optical transitions at 505 nm (2.46 eV) and 544 nm (2.28 eV) was found to increase with decreasing concentration of TBA-4 in the blends. The fact that the oscillator strength of the new optical transitions increases with increasing two-dimensional (2-D) confinement of PBZT segments confirms that they originate from exciton confinement in the PBZT *quantum wires*. The superior sensitivity of PLE spectroscopy compared to absorption spectroscopy for probing the excitonic states of semiconducting polymer quantum wires arises from the relatively small absorption but highly efficient emission by the PBZT quantum wires which act as traps for efficient excitation energy transfer from the surrounding 2,5-PBO.

Figure 2a shows the PL spectra of TBA-4 and several TBA-4/2,5-PBO blends (2,5,10, and 15%) photoexcited at 360 nm. The PL spectrum of the PBZT homopolymer thin film photoexcited at 440 nm is also included in Fig. 2a for comparison. The relatively weak emission from 2,5-PBO in the 380-430 nm region is completely quenched in TBA-4 and some of the blends (10-15%) due to efficient energy transfer. The main PL emission band in the 450-600 nm region is due to the PBZT chromophores of varying degree of confinement in the blends. Relative to the pure PBZT homopolymer, progressive 2-D confinement of excitons in the PBZT segments of TBA-4 in the blends results in blue shift and band narrowing of the PL emission. For example, the full width at

half maximum of the PL emission band is reduced from 124 nm in pure TBA-4 to 51 nm in the 2% blend (PBZT quantum wire). As shown in Fig. 2b, the relative luminescence efficiency of the PBZT quantum wires in the dilute blends (<5%) was enhanced by factors of up to 4-7 compared to pure TBA-4 or PBZT.

Figure 3 shows the relative PL emission quantum efficiency of TBA-4 and TBA-4/2,5-PBO blends photoexcited at 435 nm under applied electric fields. Field-induced PL quenching is observed to depend strongly on the concentration of TBA-4 and hence on the confinement of the PBZT chromophores. About 60-70% of the PL of the pure TBA-4 and the 25% blend is quenched at 10^6 V/cm whereas no PL quenching is observed in the quantum wires ($\leq 5\%$ blends) at fields as high as 2.8×10^6 V/cm. This excellent stability of excitons in PBZT quantum wires under high applied fields confirms their 1-D nature and the expected greater difficulty of dissociating such low dimensional excitons compared to excitons in bulk conjugated polymers or even pure block copolymers. These electric field-induced PL quenching results also have implications for light emitting diodes based on semiconducting polymers as others have also pointed out.¹⁹

In summary, we have prepared semiconducting polymer quantum wires by using our recently reported self-assembly of a triblock conjugated copolymer and a conjugated homopolymer in binary blends. Exciton confinement effects in the organic semiconductor quantum wires were observed at room temperature, including new discrete energy levels in the photoluminescence excitation spectra. Electric field-induced quenching of photoluminescence was also demonstrated as a technique for probing the confinement dimensionality of excitons in semiconducting polymers.

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Figure Captions

- Figure 1. UV-visible absorption spectrum of TBA-4 thin film and representative PLE spectra of TBA-4/2,5-PBO blends monitored at 600 nm.
- Figure 2. (a) PL spectra of TBA-4 and TBA-4/2,5-PBO blends (2-15%) excited at 360 nm and PBZT excited at 440 nm. (b) Relative PL quantum efficiency as a function of TBA-4/2,5-PBO blend composition for 435 nm excitation.
- Figure 3. Electric field-induced PL quenching of TBA-4/2,5-PBO blends at different compositions for 435 nm excitation.

FIG. 1
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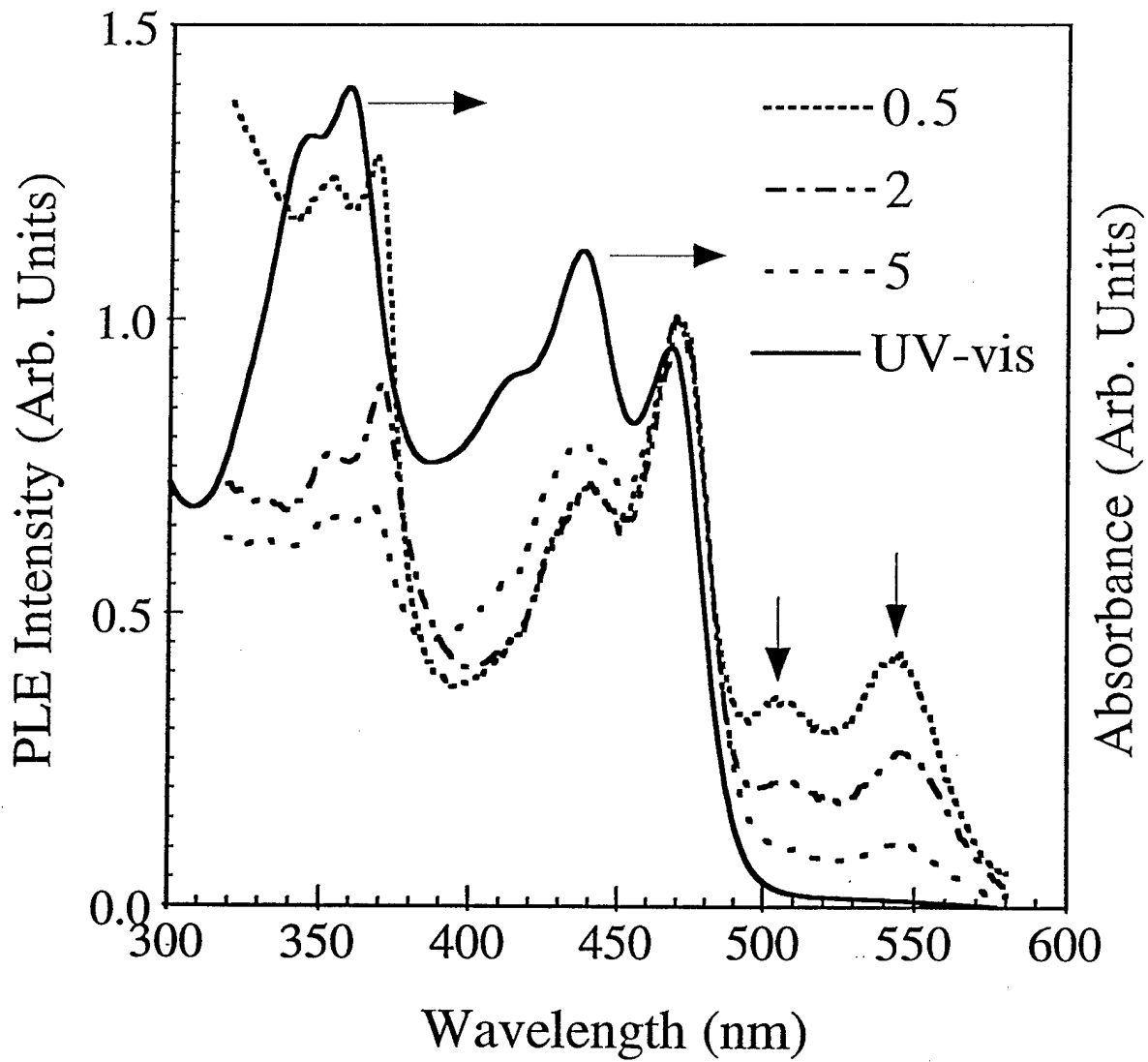


FIG. 2
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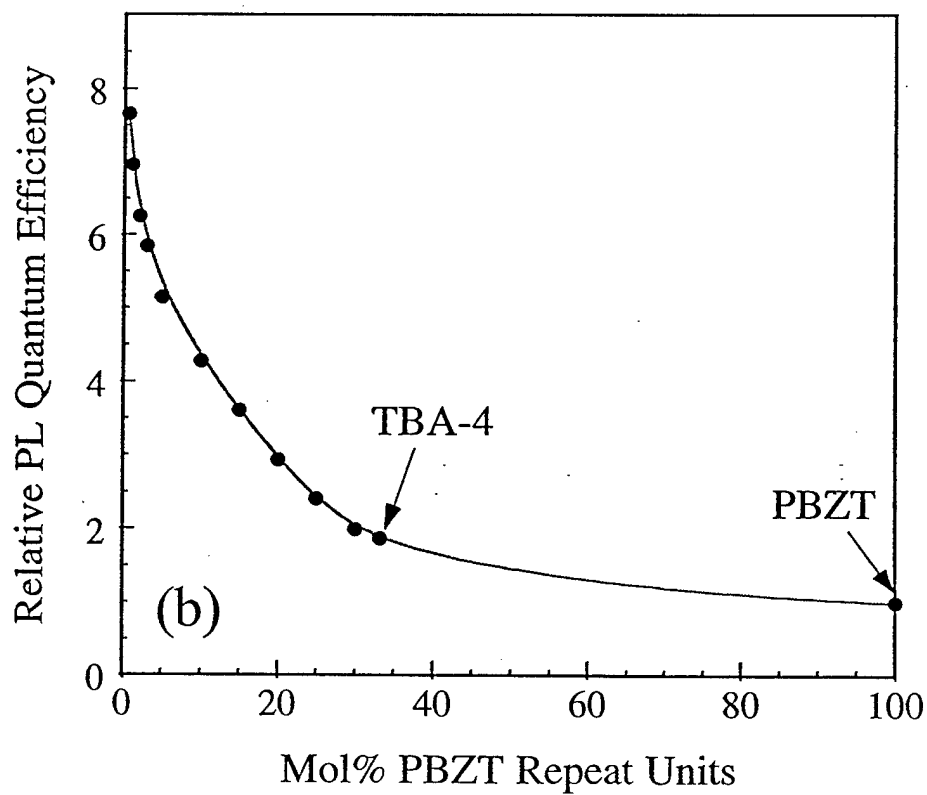
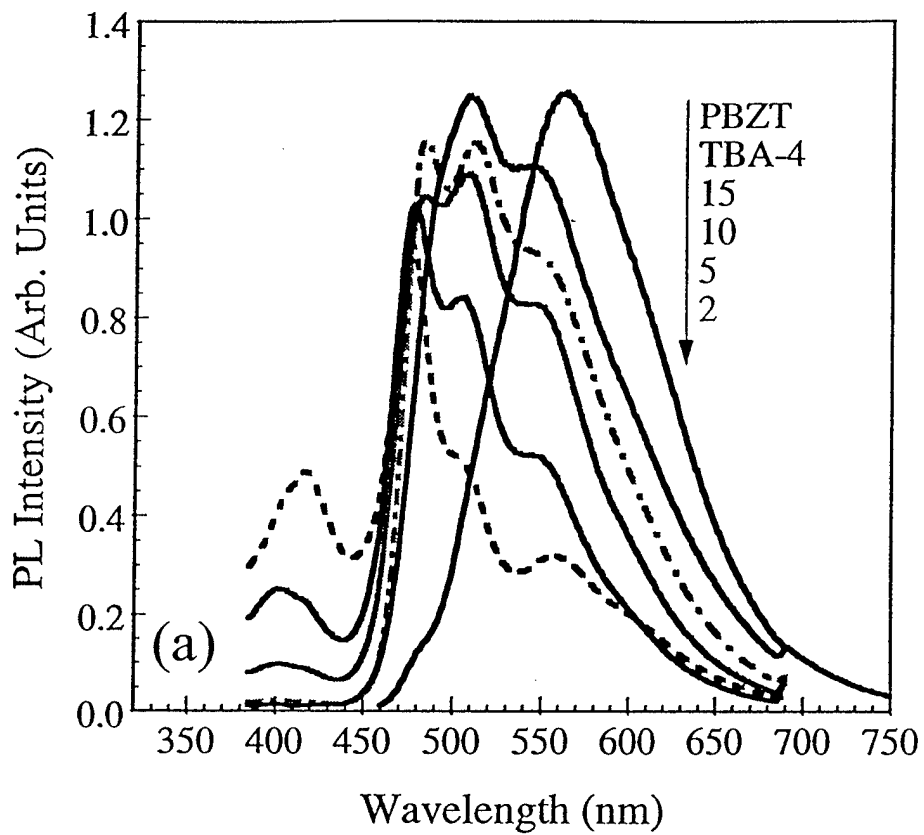


FIG. 3
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