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13. ABSTRACT (Maximum 200 words) Low dimensional organic semiconductors such as quantum boxes, quantum wires, or superlattices are predicted to exhibit enhanced or novel electronic and optical properties for applications in solid state electronic and optoelectronic devices in ways similar to low dimensional inorganic semiconductors. However, the relatively small charge carrier and excitation Bohr radii of organic semiconductors (ca. 1.0-1.5 nm) has heretofore made it difficult to prepare organic semiconductor heterostructures with quantum confinement effects. Ultrasmall semiconducting polymer quantum boxes and wires with confinement volumes of 1-2 nm ³ have been prepared in our laboratory by self-organization of blends of ABA block conjugated copolymers with a parent homopolymer. Observation of new optical transitions, enhanced luminescence, and stability of luminescence at high electric fields confirmed the confinement of excitons in the organic quantum boxes and wires.				
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SELF-ASSEMBLED ORGANIC SEMICONDUCTOR QUANTUM BOXES AND WIRES FROM BLOCK COPOLYMERS

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Low dimensional inorganic semiconductor systems have been of much scientific and technological interest in the past 25 years (1-3). Compared to bulk semiconductors, low dimensional semiconductors exhibit novel or modified electronic and optical properties due to spatial confinement of charge carriers or excitons (1-3). Increased exciton binding energy, enhanced oscillator strengths, large Stark shifts, and enhanced optical nonlinearities in low dimensional semiconductors have led to device applications such as diode lasers, Stark effect optical modulators, self-electrooptic effect devices, optical waveguide switches, and cavity-less nonlinear optical bistability (1-3). Organic semiconductors with reduced dimensionality are also of growing interest owing to their expected unique features compared to the corresponding inorganic semiconductors (4-8). Defect-free heterostructures can be more readily fabricated due to the weak Van der Waals interactions between organic molecules. The smaller dielectric constant of organic molecules and polymers [-3-4] compared to inorganic semiconductors [>10] could result in strong Coulomb interaction between electrons and holes, leading to strong excitonic effects and large exciton binding energies [-0.5-1.0 eV].

To achieve quantum confinement effects in a semiconductor heterostructure requires that the size of the potential well structure be comparable or smaller than the charge carrier or exciton Bohr radius in at least one spatial direction (1,3). Exciton Bohr radii (a_B) in bulk organic semiconductors are generally small, ca. 10-15Å, for example: 12-13Å in 3,4,9,10-perylenetetracarboxylic dianhydride(4); 10-12Å in various single crystal polydiacetylenes; 13Å in poly(benzobisthiazole-1,4-phenylene)(9). This size requirement places a severe limitation on the possible methods that could be used to prepare low dimensional organic semiconductor systems. To date, two conceptual approaches to the preparation of organic semiconductor quantum structures have been explored: (i) ultrahigh vacuum organic molecular beam deposition of layered heterostructures from small molecules(7); and (ii) heterostructured semiconducting polymers via block copolymerization(5-8). Although there have been many theoretical calculations predicting quantum confinement effects in block conjugated copolymer chains (5,6), this approach has so far not resulted in experimental realization (7,8,10) of quantum confined nanostructures in semiconducting polymers. The prior synthetic difficulty of preparing well-defined block conjugated copolymer heterostructures in which to test theoretical predictions was recently overcome by the synthesis of a soluble and processible ABA triblock copolymer in our laboratory (10). However, our extensive studies of the block conjugated copolymer heterostructures did not reveal any evidence of the predicted quantum confinement effects (10).

We report here a novel approach to preparing zero- and one-dimensional organic semiconductor systems and experimental observation of the associated quantum confinement effects. The approach exploits the self-organization of blends of an ABA copolymer with its parent homopolymer A to prepare isolated boxes and wires of the middle block B with uniform rectangular cross-sectional area of a single molecular chain.

EXPERIMENTAL SECTION

As many theoretical studies have suggested (5,6), an $A_n B_m A_n$ block conjugated copolymer chain constructed from two different

semiconducting polymers A_n and B_m with optical band gaps E_g^A and E_g^B , respectively, where $E_g^A > E_g^B$, represents a quantum-well structure with electron potential barrier of $\Delta E_g = E_g^A - E_g^B$. Thin films of such a triblock copolymer with an average composition $A_{20}B_9A_{20}$ (TBA-1, Fig.1a) where A and B are the repeat units of poly(benzobisthiazole-1,4-phenylene) (PBZT) and poly(2,5-benzoxazole) (2,5-PBO), respectively, were shown to be microphase separated (10), resulting in ordered aggregation of block copolymer chains (Fig.1b). The sizes of the PBZT microdomains in the microphase separated block copolymer can be expected to significantly exceed the bulk exciton Bohr radius of PBZT ($a_B = 13\text{\AA}$) and hence the absence of any quantum confinement effects (10). To overcome microphase separation, we propose that self-organization of suitable mixtures of a triblock copolymer with its component homopolymer 2,5-PBO will result in heterostructures in which three-dimensionally confined PBZT quantum boxes are well defined with ΔE_g of 0.81eV (Fig.1c). From the X-ray data for the homopolymers (10), such PBZT quantum boxes (Fig.1c) have the precise cross-sectional area of $(0.35 \times 0.58) \text{ nm}^2$ and a length l_m which varies with the number of PBZT repeat units incorporated into the B_m block. For TBA-1 the average l_m is 11 nm; for another triblock TBA-3 with composition $A_{25}B_4A_{25}$, $l_m = 5$ nm. The cross-sectional area of 0.203 nm^2 is a factor of 8.3 smaller than a_B^2 which implies very strong exciton confinement in two spatial directions; furthermore, the 3-D confinement volumes of the PBZT boxes in isolated TBA-1 and TBA-3 chains are $1.01\text{-}2.33 \text{ nm}^3$ compared to $a_B^3 = 2.20 \text{ nm}^3$. Thus, the proposed approach can produce heterostructures suitable for investigating quantum confinement phenomena.

The detailed synthesis and characterization of the homopolymers and block copolymers investigated here have been reported(10,11). Blends of various compositions of TBA-1/2,5-PBO and TBA-3/2,5-PBO were prepared in nitromethane/ GaCl_3 solution and thin films were prepared by spin coating onto silica or indium-tin-oxide (ITO) coated substrates, using methods previously described for the pure copolymers and homopolymers (10,11). The film thickness of the samples was typically 100 nm and was measured by an Alpha Step Profilometer (Tencor Instruments) which has a resolution of 1 nm. Photoluminescence (PL) and electric field-induced PL quenching measurements were done by using a Spex Fluorolog-2 Spectrofluorimeter. Thin films were positioned such that the emission was detected at 22.5° from the incident radiation beam. For PL measurement under an external field, aluminum was evaporated onto thin film samples on indium-tin-oxide (ITO) coated glass. A positive bias voltage was applied to the ITO electrode, creating an electric field across the film sandwiched between ITO and aluminum electrodes. The samples were illuminated through the ITO-glass side and the PL spectra collected under applied field. Time-resolved (ps) PL decay measurement were performed by using time-correlated single photon counting technique described elsewhere (J.A. Osaheni and S.A. Jenekhe, *J. Am. Chem. Soc.* **117**, 7389 (1995)).

RESULTS AND DISCUSSION

Photoluminescence (PL) spectroscopy at 298K was very sensitive in revealing evidence of progressive spatial confinement in going from the pure triblock to blends containing 1 triblock chain per 1-29 2,5-PBO chains. The PL emission spectra of thin films of TBA-1 and TBA-1/2,5-PBO blends excited at 340 nm are shown in Fig.2. Also shown for comparison is the emission spectrum of the PBZT homopolymer excited at 440 nm. It has previously been established that the broad and featureless PL spectrum of PBZT centered at 563 nm originates from interchain excimer emission (12). The PL spectrum of the pure TBA-1 is also broad, nearly featureless; blue shifted from that of pure PBZT, and can be similarly interpreted as originating from excimer emission from the

microphase separated PBZT block. Progressive dispersion of TBA-1 in 2,5-PBO matrix in the blends from 15 to 3 mol% results in band narrowing and slight blue shift of a more structured band compared to the pure TBA-1. The negligible Stokes shift in the dilute blends indicates that the photogenerated excitons are confined to the lowest excited state. The small emission band at 380-430 nm is from the 2,5-PBO matrix. For all the blends, no variation of the PL spectra was observed upon varying the excitation wavelength from 320 nm to 440 nm. This means that even the preferential excitation of the 2,5-PBO matrix in the 320-380 nm region results in efficient energy transfer to the spatially confined PBZT quantum boxes which act as exciton traps and radiative recombination centers.

Photoluminescence excitation (PLE) spectroscopy has been widely used as one of the most sensitive probes of the discrete exciton states in low dimensional inorganic semiconductor systems (3). The room temperature (298K) PLE spectra of thin films of TBA-1 and a TBA-1/2,5-PBO blend are shown in Fig. 3. These PLE spectra were obtained by monitoring the emission at 600 nm where there is negligible emission from the 2,5-PBO chromophore. The PLE spectra of TBA-1 and blends have features similar to the absorption spectra as well as major differences. The presence of a large 340-360 nm band due to 2,5-PBO absorption shows that the 600-nm emission from the PBZT block contains a significant contribution from excitation energy transfer from 2,5-PBO. The PLE spectrum of TBA-1 is similar to its absorption spectrum. Dilution of the PBZT block concentration in the blends, hence improved quantum box confinement, reveals clear peaks at 505 (2.46 eV) and 544 nm in the PLE spectra. In blends of 0.5-1.0%, additional new discrete peaks appear in the PLE spectra at 311 nm (3.99eV), 325 nm (3.82 eV), 392 nm (3.16 eV) and 422 nm (2.94 eV). This observation of several new optical transitions in the PLE spectra of PBZT quantum boxes provides the first direct evidence of quantum confined exciton states in an organic semiconductor system.

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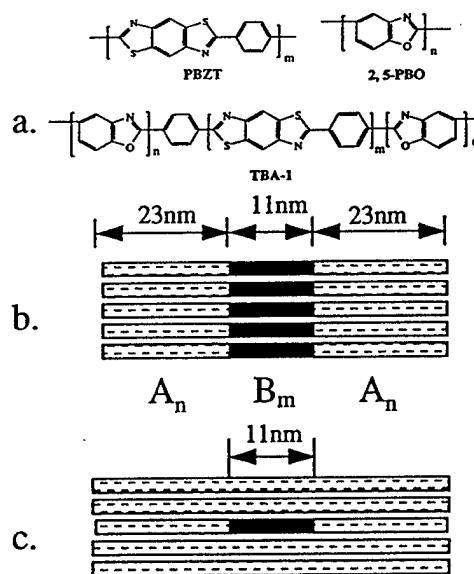


Figure 1. Self-assembling approach to organic semiconductor quantum boxes and wires: chemical structures of materials(a), microphase separation of ABA triblock(b), and self-organized blend of triblock with homopolymer.

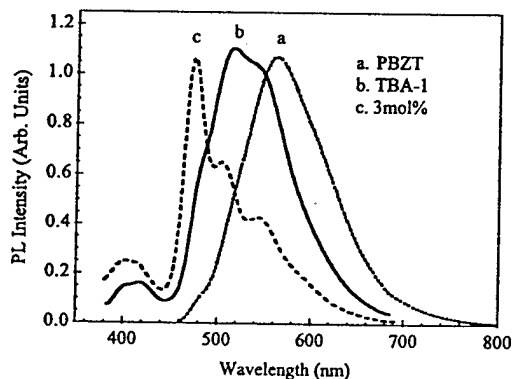


Figure 2. Photoluminescence (PL) spectra of thin films.

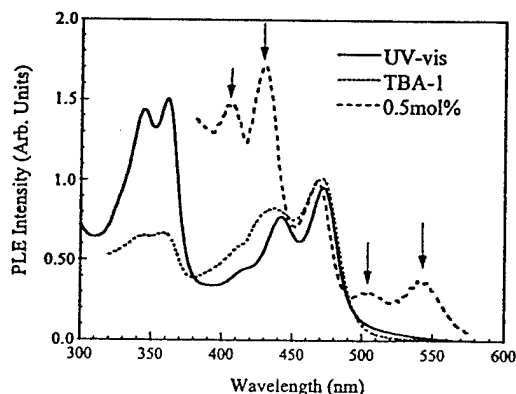


Figure 3. Photoluminescence excitation (PLE) spectra of thin films of TBA-1 and TBA-1/2,5-PBO blend. Arrows indicate new peaks.