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Research Article

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## Absorption spectra binary blends of PQ

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### ABSTRACT

Large enhancement in electroluminescence efficiency and brightness of light-emitting diodes fabricated from binary blends of conjugated polyquinolines was observed compared to devices made from the homopolymers. Blends of poly(2,2-(2,5-thienylene)-6,6-bis(4-phenylquinoline)) (PTPQ) and poly(2,2-(biphenylene)-6,6-bis(4-phenylquinoline)) (PBPQ), for example, had EL efficiency and luminance of up to a factor of 30 enhancement. These results demonstrate new phenomena in the electroluminescence and photophysics of multicomponent conjugated polymers.

**Keywords:** Binary blends of PTPQ and PBPQ

### ARTICLE INFO

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### 1. Introduction

Electroluminescence (EL) from blends of conjugated polymers has been described in several recent reports. Voltage-tunable electroluminescence color was observed in phase-separated blends of several Polythiophene derivatives having different emission colors. Phase separation of the International Journal of Chemistry and Pharmaceutical Sciences

blends on the 50-200 nm scale, which is comparable to or larger than the emitter thickness in the devices, was essential to the multicolor LED emission. White light EL emission has been observed from ternary blends of poly(3-(4-octylphenyl)-2,2 $\phi$ -bithiophene), poly(3-methyl-4-octyl

thiophene), and poly(3-cyclohexylthiophene),13a from binary blends of Poly(2-methoxy-5-(2-ethylhexoxy)-1,4-phenylenevinylene) (MEH-PPV) with an alkoxy (trifluoromethyl)-stilbene-substituted poly(methyl acrylate) derivative (CF<sub>3</sub>-PMA),12c from blends of a ladder-type poly (*p*-phenylene) (*m*-LPPP) with poly (perylene-*co*-diethyl benzene) (PPDB),13b and from ternary blends of polyquinolines. Enhancement in EL quantum efficiency and luminance of LEDs made from blends, compared to the component polymers, has been reported. Blends of poly-(3-hexylthiophene) (P3HT) and MEH-PPV,7b blends of MEH-PPV and a conjugated-nonconjugated multi block copolymer (CNMBC), poly (1,3-propanedioxy-1,4-phenylene-1, 2-ethylene(2, 5-bis (trimethylsilyl)-1, 4-phenylene) -1, 2-ethenylene-1,4-phenylene), 7c were reported to have enhanced EL efficiency.

## 2. Materials and Methods

**Materials:** The polyquinolines used in this study had intrinsic viscosities of 3-12 dL/g, which were measured in 0.1 mol % di-*m*-cresyl-phosphate/*m*-cresol at 25°C or in methanesulfonic acid at 30°C, indicating that they are high molecular weight polymeric materials. Since all the polyquinolines are good electron transport (n-type) and emissive materials, their electroluminescence was investigated in a bilayer device structure including a hole transport layer consisting of 1,1-bis(di-4 tolylamino)phenyl cyclohexane (TAPC) dispersed in polystyrene (PS).

## 3. Results and Discussion

### Electronic Structures of Polyquinolines.

Figure 1a shows the optical absorption spectra of Polyquinoline thin films. Bu-PPQ, PPPQ, and PBPQ have very close absorption peaks and band gaps due to their structural similarities. However, Bu-PQ and PTPQ show bathochromic shifts in both the absorption peaks and band gaps. For example, Bu-PPQ and PPPQ have absorption peaks at 399 and 400 nm, respectively, and the same band gap of 2.78 eV. PBPQ has an absorption peak at 405 nm and a band gap of 2.81 eV. Bu-PQ has an absorption peak at 412 nm and a band gap of 2.65 eV. PTPQ has an absorption peak at 471 nm and a band gap of 2.49 eV. The relative HOMO and LUMO levels of these polyquinolines can be represented by their oxidation and reduction potentials.

### Optical Absorption Spectra.

The optical absorption spectra of thin films of PTPQ, PBPQ, and their blends are shown in Figure 3b. PBPQ has an absorption peak at 405 nm and an absorption band edge around 441 nm (2.81 eV). PTPQ has an absorption peak at 475 nm and an absorption band edge around 506 nm (2.49 eV). The absorption spectra of the blends are almost identical to that of PBPQ at low concentrations (0.1-1%) of PTPQ. However, at higher concentrations (5-50%) of PTPQ, the absorption band of PTPQ clearly shows up as a lower energy shoulder in the absorption spectra of the blends. The absorption spectra of the binary blends are simple superposition of those of PBPQ and PTPQ. New absorption features were not observed in the wave length range of 200-2800 nm, suggesting that the two blend components have no observable interactions in their

electronic ground states. Similar results were observed in Bu-PQ: PBPQ, Bu-PQ:Bu-PPQ, and PPPQ:Bu-PPQ blends. The optical absorption spectra of bilayer films of the blends or homopolymers with the hole-transport layer TAPC:PS used in LED devices were also measured. Figure 1c shows such a representative spectrum of PBPQ/TAPC:PS bilayer along with those of the PBPQ and TAPC:PS single layers. The spectrum of the PBPQ/TAPC:PS bilayer is a simple superposition of those of PBPQ and TAPC:PS single layers, indicating that there is no complex formation between PBPQ and TAPC in their ground states. Similar results were found for bilayers of other polyquinolines or blends with TAPC: PS.

### Photoluminescence

PL spectra of thin films of the polyquinolines investigated are shown in Figure 2a. The PL emission colors of these polyquinolines are green-yellow (Bu-PPQ), orange (Bu-PQ, PPPQ, and PBPQ), and red (PTPQ). These polymers showed structureless PL emission spectra with a large Stokes shift ranging from 139 nm for Bu-PPQ to 171 nm for PPPQ. The broad, featureless PL emission spectra and the large Stokes shifts of these polyquinolines are characteristic of intermolecular excimer emission which has previously been observed in many conjugated polymers and self-organized block copolymers containing polyquinolines. However, the single-chain emission of even excimer-forming conjugated polymers can usually be observed in dilute fluid or solid solutions. Figure 2b shows the PL emission spectra of PBPQ and PTPQ in an inert poly (methyl methacrylate) (PMMA) solid matrix (1 wt %). The PL emission spectrum of PBPQ in PMMA has a peak at 432 nm and a shoulder around 450 nm. The PL emission spectrum of the 1 wt % PTPQ: PMMA, on the other hand, has a peak at 464 nm and a shoulder around 500 nm. These more structured PL spectra of PBPQ and PTPQ exhibit very small Stokes shifts and can be assigned to the single-chain emission (singlet intrachain excitons) of the polymers.

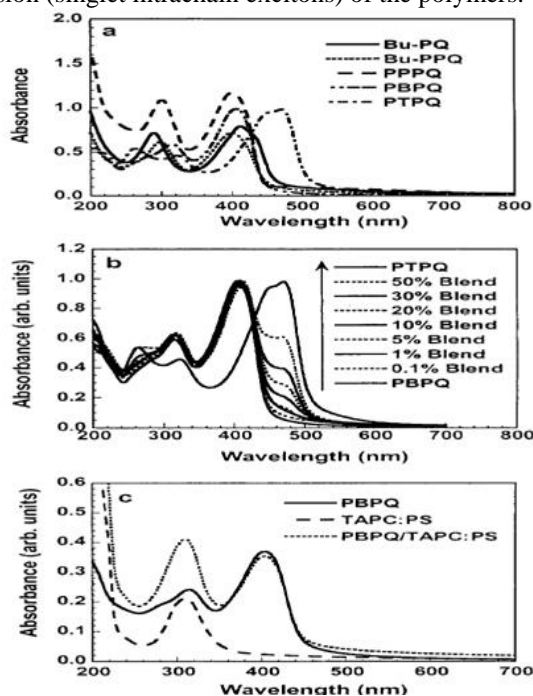
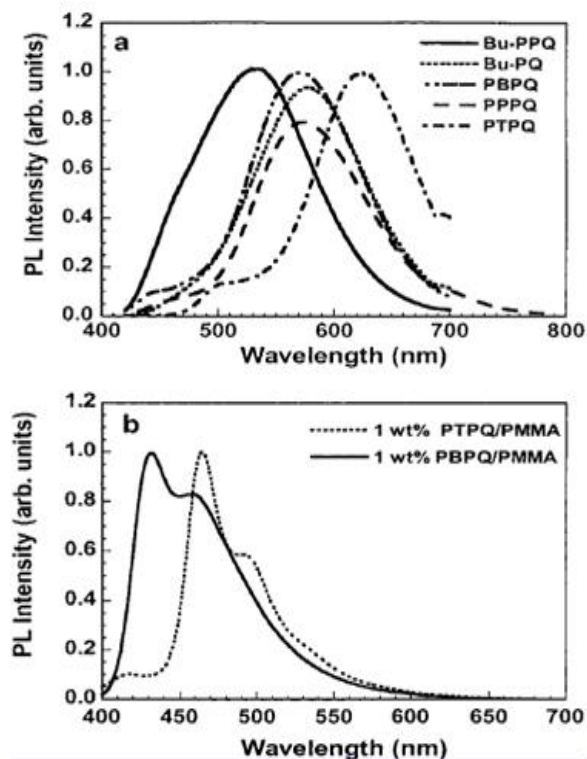


Figure 1: Optical absorption spectra of thin films on silica

Substrates: (a) poly quinoline homopolymers; (b) PTPQ, PBPQ, and their blends; (c) PBPQ, TAPC: PS, and PBPQ/TAPC: PS



**Figure 2:** PL spectra of thin films: (a) poly quinoline homopolymers ;(b) PTPQ and PBPQ dispersed in PMMA. The excitation wavelength was 400 nm for all spectra except those of PTPQ (430 nm).

#### 4. Conclusion

These results have implications for designing and developing new supramolecular materials for electronic, optoelectronic, and photonic applications using multicomponent conjugated polymers. We expect that there will be even larger enhancement of the EL of polymer blends if both exciton confinement and excitation energy transfer could be facilitated. Electroluminescence of binary blends of conjugated polyquinolines was investigated using four different model blend systems of PTPQ: PBPQ, Bu-PQ: PBPQ, Bu-PQ:Bu-PPQ, and PPPQ: Bu-PPQ. A 3-30 times enhancement of EL efficiency and LED brightness of the blends compared to those of the homopolymers was observed. From the estimated HOMO/LUMO energy levels of the component polymers, the current-voltage characteristics of the EL devices, and the results of electric-field-modulated photoluminescence spectroscopy, we conclude that the observed EL enhancement in the blends originates primarily from the spatial confinement of excitons which leads to improved exciton stability and electron-hole recombination efficiency.

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