The Structure-Property Relationship of Conjugated Polymers: the Effect of Heteroaromatic Rings and Connectivity on Photophysical Properties.

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INTRODUCTION

Polymer light-emitting devices have attracted attention because of their potential utility in a wide variety of flat-panel display applications. To be used as such, polymers must emit colors of interest and have high emission intensities. The emission can be tuned by varying the bandgap of the polymer. The HOMO-LUMO gap of the polymer is related to the extent of conjugation of the π-electrons. The efficiency of emission can be reduced due to inter-chain interactions such as excimer and aggregate formation. In order to design better polymers a comprehensive understanding of the relationship between structure and the resultant properties of the polymer is required.

Poly(paraphenylene)s (**PPP**) have been reported in literature as blue-emitting polymers.[1] In this present study the effect of heteroatoms along the polymer backbone similar to PPP was studied using the electron-deficient polymers: poly(2,5-didecoxyphenyl-5,5'-bipyridine) (**PBP_55'**), poly(2,5-didecoxyphenyl-4,4'-bipyridine) (**PBP_44'**), and poly(2,5-didecoxyphenyl-5,5'-bithiazole) (**PTA**). Through their bipyridine and thiazole moieties, these polymers have the ability to chelate to metals ions which enable them to be used in metal ion sensing or as efficient sensitizers.

One electron-rich polymer was studied, namely poly(2,5-didecoxyphenyl-2,3-thiophene) (**PT_23**). To achieve high-energy polymers, the thiophene moieties were attached from 2,3-positions as opposed to widely published 2,5-positions. Electron rich polymers are important because they can be used as hole transport layers in light-emitting devices. The repeating units of the polymers are shown in Figure 1.
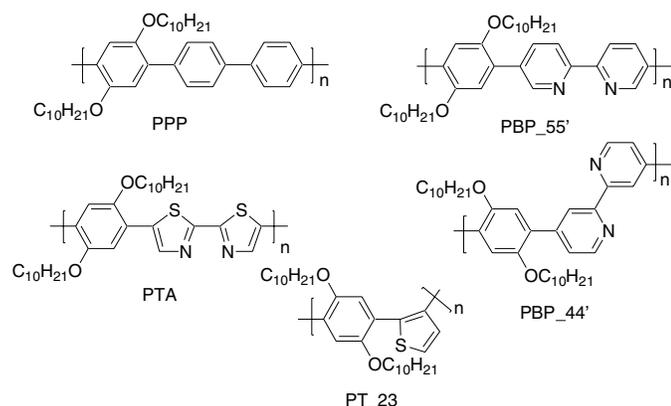
Figure 1. The structures of the polymers: PPP, PBP_55', PBP_44', PTA, and PT_23.

This study describes the synthesis and photophysical investigation of a series of blue-emitting polymers. The effect of heteroatoms in the polymer backbone, as well as that of the polymer architecture on emission properties, singlet energies, and triplet energies are discussed.

EXPERIMENTAL

Reagents. All starting materials and solvents were purchased from Sigma-Aldrich. The monomers 5,5'-diiodo-2,2'-bipyridine,[2] 4,4'-dibromo-2,2'-bipyridine,[3] 5,5'-dibromo-2,2'-bithiazole,[4] and 2,5-didecoxyphenyl-1,3-bisboronic acid[5] were prepared using published procedures.

Polymerization of the bisboronic acid with its corresponding dihaloarene was carried out by palladium(0)-mediated Suzuki coupling to obtain the desired polymers.[6]

Polymerizations. 2,5-didecoxyphenyl-1,3-bisboronic acid (0.001mol) and corresponding dihaloarene (0.001mol) was placed in an argon-flushed flask. THF (15mL) and 1M aqueous Na_2CO_3 (15mL) were added, degassed, and brought to reflux under argon. Palladium catalyst (35mg) dissolved in THF (5mL) was added and the reaction was refluxed for 2 days. The organic phase was added to methanol, producing the polymer as a solid precipitate, which was further purified by reprecipitation in methanol.

Photophysical Measurements. Steady state emission spectra were recorded using a Fluorolog-3 model FL3-21 with a 450W xenon lamp source, double grating excitation monochromator, single grating emission monochromator, and a room temperature R928 PMT serving as the detector. Phosphorescence studies were carried out using the 1934D3 phosphorimeter in conjunction with the Fluorolog-3 system with a xenon flash lamp. Plots were generated using GRAMS/32 and DataMax software. Absorbance spectra were generated using Cary 14 OLIS UV/Vis/NIR Spectrophotometer equipped with deuterium and tungsten lamps for UV and Vis/NIR regions.

RESULTS AND DISCUSSION

Upon photoexcitation, polymers will form excited states. The most commonly seen has been singlet states, which give rise to fluorescence, along with triplet states and inter-chain interactions. The triplet state is important in phosphorescence or triplet sensitization, and is formed by the intersystem crossing of the singlet state. Inter-chain interactions give rise to excimer, exciplex or aggregate formation, all of which are competitive pathways for deexcitation and result in reduction of fluorescence.

Table 1. The Absorbance Maxima, Emission Maxima, FWHM of Emission, and the Stokes Shift (Δ) in Solution.

Polymer	Abs. Max. (nm)	Em. Max. (nm)	FWHM (nm)	Δ (cm⁻¹)
PPP	350	412	57	4,137
PBP_55'	370	430	78	3,771
PBP_44'	340	418	60	5,488
PTA	461	516	70	2,312
PT_23	346	463	81	7,303

The properties of fluorescence arising from the singlet exciton are displayed in Table 1. Upon changing a biphenyl group in PPP to a 5,5'-bipyridine or 5,5'-thiazole group, the absorbance maximum was shifted to lower energy by 20nm and 110nm, respectively. Conversely, the use of a 4,4'-bipyridine group shifted the absorbance maximum towards high energy. The emission maximum of the polymers followed similar trends.

PT_23 polymers absorbed around 345 nm and its emission maximum was at 463nm. PT_23's large FWHM and larger Stokes shift strongly suggested the existence of a larger vibrational manifold. In contrast, the polymer PTA had a small Stokes shift indicating less structural relaxation. PBP_44' had more vibronic structure than PBP_55' indicating latter is more rigid. The pronounced low energy tail for polymers PBP_55' and PTA was indicative of inter-chain interactions.

All of the polymers showed no phosphorescence at room temperature. However, upon cooling the solution to low temperatures, phosphorescence was observed. The low temperature phosphorescence scans showed two peaks, as seen in Figure 2. The high-energy, fast-relaxing band was attributed to delayed fluorescence, while the second low-energy, slow-relaxing band was phosphorescence. Delayed fluorescence can arise from two processes: thermal reversion of triplets to singlets, and triplet-triplet annihilation. Considering the high singlet-triplet energy gap and the low temperature the studies were carried out in, delayed fluorescence due thermal reversion can be ruled out. Since these polymers have low rates for phosphorescence and higher triplet life times, triplet-triplet annihilation is more probable.
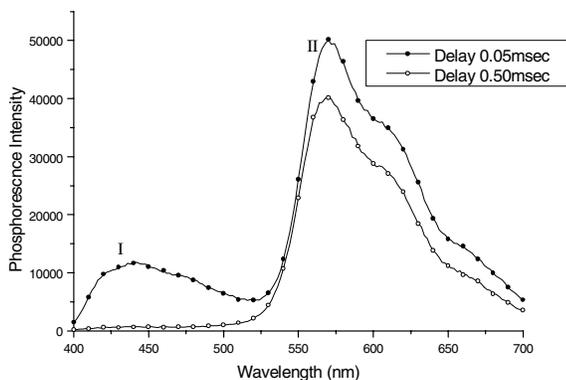
Figure 2. Delayed emission spectra for the polymers at low temperatures.

The emission spectra of PBP_55' and PTA consist of a higher energy emission peak and a lower energy tail. These lower energy tails are indicative of inter-chain interactions, such as excimer formation or aggregate formation. The excimers are formed by interaction of an excited state molecule with another in its ground state, allowing for the electronic wavefunction to be delocalized over two molecules in the excited state. Aggregates though are formed by the interaction of two or more molecules in the ground state, with the electronic wave function delocalized over these molecules in the ground state as well as in its excited state. The direct result of this was an additional absorbance peak in lower energies.
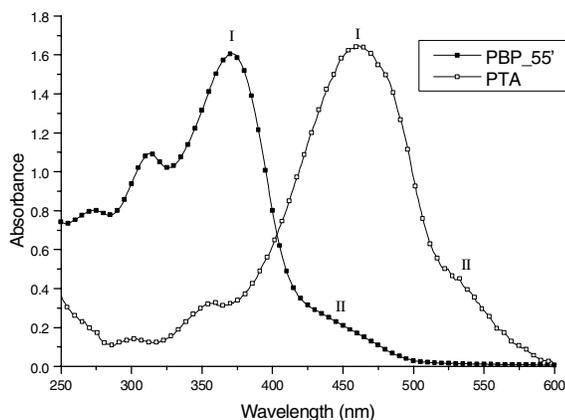
Figure 3. The absorbance spectra of polymers in chloroform, indicating aggregate absorption.

The absorbance spectra of PBP_55' and PTA, given in Figure 3, with each having two regions. For each, band I corresponds to the polymer absorbance maximum, and band II which is lower in energy and not seen in solvents such as toluene but seen in chloroform and THF. The appearance of the second band indicates that in both polymers aggregates are formed. This is similar to previous phenomena seen in polypyridines.[7] Aggregates can be excited optically. Upon exciting the polymers PBP_55' and PTA at band II, they produced emission centered around 505nm and 565nm, respectively. The energies of these emission bands correspond to the low energy tails observed in emission spectra.

Table 2. State Energies of the Polymers.

Polymer	E_S cm^{-1} (eV)	E_T cm^{-1} (eV)	dE_{ST} cm^{-1} (eV)
PPP	25,907 (3.21)	19,920 (2.47)	0.74
PBP_55'	24,938 (3.09)	17,668 (2.19)	0.90
PBP_44'	26,205 (3.25)	18,868 (2.34)	0.91

The singlet and triplet energies of the polymers are shown in Table 2. By changing the biphenyl group in PPP to a bipyridine group in PBP_55', the energies were reduced. The lowering of the band gap by the electron deficient bipyridine can be attributed to donor-acceptor interactions between the two monomer units. The connectivity of the bipyridine group played a major role in the energetics of the polymer as seen when comparing PBP_55' and PBP_44'. The latter has higher energy due to the kinks introduced to the polymer chain and/or cross conjugation through these segments.

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