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Comparison of Optical Properties between Blue-Emitting Poly(*m*-phenylenevinylene) and PPV Block Copolymer

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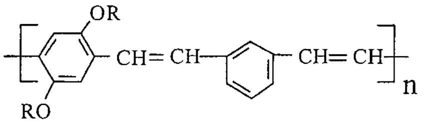
Introduction

π-Conjugated polymers with band gaps in the visible region such as poly(*p*-phenylenevinylene) (PPV) and its derivatives have attracted significant attention over the past decade, because of their potential applications in light-emitting diodes (LEDs)[1,2] and lasers.[3,4] The emission color (or the band gap) of the materials can be tuned by various means, including attachment of substituents[5] on the polymer backbone (through both steric and electronic influence), introduction of *m*-phenylene linkages,[6] and inclusion of nonconjugated carbon bridges[7] along the polymer backbone.

Our recent studies[6b] show that inclusion of an *m*-phenylene bridge along the poly(phenylenevinylene) (PPV) backbone effectively interrupts the π-conjugation, leaving a well-defined chromophore sandwiched between the two adjacent *m*-phenylene units. By using low-temperature UV−vis and fluorescence spectroscopy, the vibronic structures[8] of the electronic absorption and emission band structures in PPV **1** are found to be remarkably similar to that of its chromophore model compound **2**. Substitution of the *p*-phenylene unit in **1** by an *m*-phenylene unit[9] leads to a highly blue-emitting polymer **3**, as a result of reduced conjugation length. This feature of predictable color control through the *m*-phenylene resembles that using a nonconjugated carbon bridges as shown in **4**, in which the oligomeric PPV chromophore is isolated by a flexible oligo(methylene) spacer to maintain its optical characteristics. To further evaluate the function of π-conjugation interruption by *m*-phenylene, it is interesting to compare the optical properties of blue-emitting polymers **3** and **4**. The results obtained provides a useful guide for future material development. In this contribution, we report such a comparison of electronic structures by using the absorption and emission spectroscopy at variable temperature.

Results and Discussion

Solution Optical Properties of 4. UV−vis absorption of **4** in THF (Figure 1) shows a major absorption peak at 372 nm and a shoulder at about 391 nm. As the temperature is lowered, the vibronic structure becomes more and more pronounced, a feature attributed to the reduced rotational mobility and increased solvent viscosity. At −108 °C, three absorption bands were detected at 360, 377, and 399 nm (27 778, 26 525, and 25 063 cm^{-1}). The vibrational energy levels in the excited state of **4** (observed from its absorption spectrum), therefore, were separated by about 1462 cm^{-1}. It was noted that the absorption peak was slightly red-shifted ($\Delta\lambda_{max} \approx 6$ nm) when the temperature was decreased from 25 to −108 °C. A similar spectroscopic red shift was also observed in the fluorescence spectra ($\Delta\lambda_{max} \approx 8$ nm) in the same range of temperatures, indicating that the chromophore adopts a more planar conformation.



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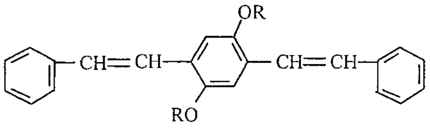

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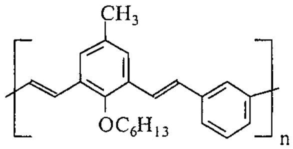

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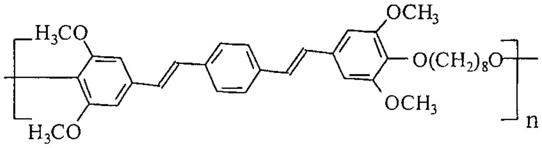

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The fluorescence spectrum of **4** in THF (Figure 2) at room temperature revealed a shoulder at ~ 413 nm and a major emission band at 437 nm. As the temperature was decreased to −108 °C, the vibronic structure again became more pronounced. To further resolve the hidden vibronic bands, the solution was cooled to −198 °C in liquid nitrogen to freeze the chromophore molecule in

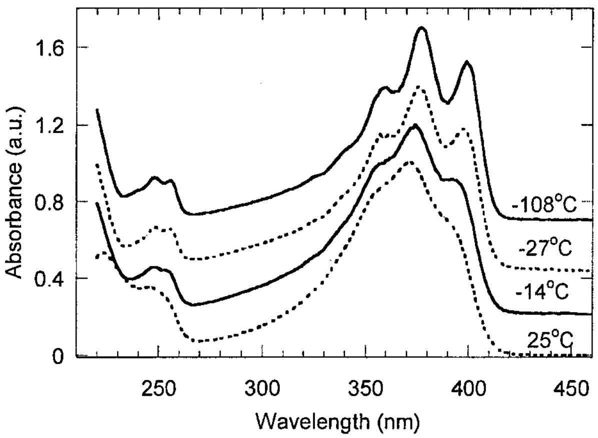

Figure 1. UV−vis spectra of blue-emitting PPV block copolymer **4** in THF at different temperatures. The spectra are slightly offset for clarity.

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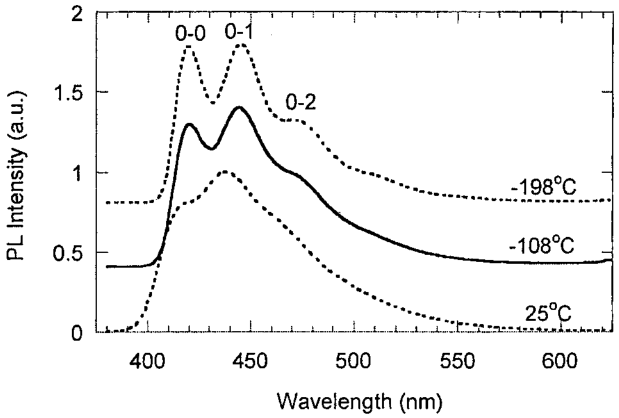


Figure 2. PL spectra of blue-emitting PPV block copolymer **4** in THF at 25, −108, and −198 °C. The spectrum at −198 °C was acquired from a frozen solution in THF.

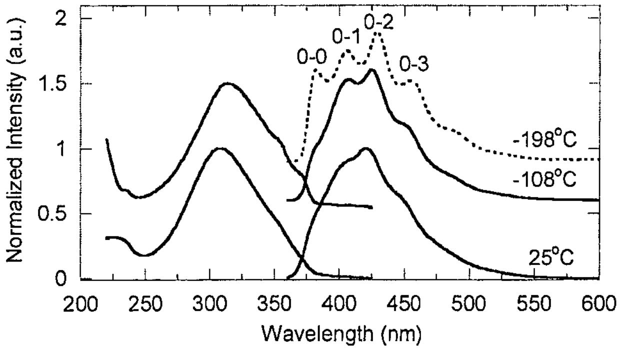


Figure 3. UV−vis and PL spectra of polymer **3** in THF at 25 and −108 °C (solid line). The PL spectrum at −198 °C (dotted line) reveals clear vibronic structure. The spectra are offset for clarity.

the solvent matrix. Three vibronic bands were observed at −198 °C with emission λ_{max} at 419, 445, and ~474 nm (23 866, 22 472, and 21 097 cm^{-1}). The vibrational energy levels in the ground state of **4** (shown from the emission spectrum) appeared to be about equally spaced with a wavenumber separation of ~1394 cm^{-1}, which is expected from a theoretical model[10] of an anharmonic oscillator. From the spectral data at −108 °C, the emission band of the highest energy ($\lambda_{max} = 419$ nm) was separated from the absorption band of the lowest energy ($\lambda_{max} = 399$ nm) by only 1197 cm^{-1}, which is smaller than the required energy gap of at least 1394 cm^{-1} for a lower energy level in an anharmonic oscillator model. The emission bands at 419, 445, and 475 nm, therefore, are probably attributable to 0-0, 0−1, and 0−2 transitions, respectively. In addition, the emission intensity from the 0−0 transition is notably increased as the temperature decreases. Clearly, the chromophore molecule in the frozen rigid environment has much less room for motion, thereby forcing an excited molecule to adopt a molecular geometry that is more similar to its ground state.

Solution Optical Properties of 3. The UV−vis absorption spectrum of polymer **3** at room temperature exhibited a major band ($\lambda_{max} = 307$ nm) with a long tail up to 382 nm (Figure 3). As the temperature was lowered to −108 °C, two shoulders at about 355 and 373 nm were detected, indicating the possible presence of the hidden vibronic bands. Attempts to further resolve the vibronic bands were not successful, due to an inability to prepare a transparent sample solution at the lowest temperature (−198 °C). On the basis of the two shoulders seen at ~355 and ~373 nm (corresponding to 28 169 and 26 810 cm^{-1}, respectively), the vibrational energy gap in the excited state of **3** is estimated to be about 1359 cm^{-1}, which is slightly smaller than the 1462 cm^{-1} for **4**. The absorption λ_{max} of **3** was similarly red-shifted ($\Delta\lambda \approx 7$ nm) as that of **4**, when the temperature was decreased from 25 to −108 °C, supporting the assumption that the chromophore adopted a more planar conformation at the lower temperature.

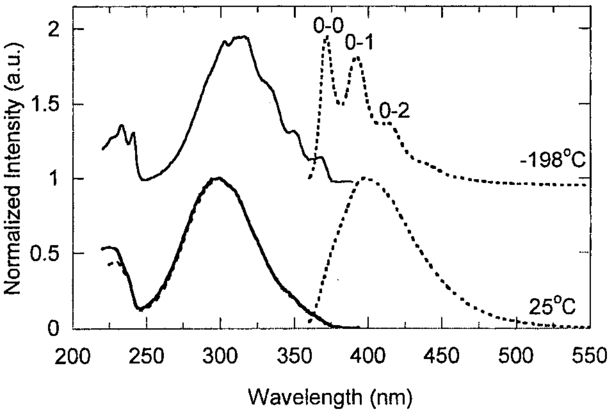
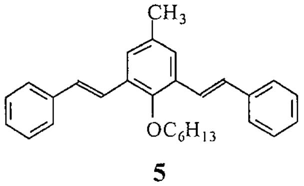


Figure 4. UV−vis (solid line) and fluorescence (dotted line) spectra of **5** in a solvent mixture of diethyl ether, ethanol, and 2-methylbutane at 25 and −198 °C. The UV−vis absorption spectrum in methanol (dotted line) exhibits the same profile as in the solvent mixture.

The presence of hidden vibronic structure in the UV−vis absorption spectrum of **3** was further confirmed by examining a model compound, 1,3-bis(2-phenylvinyl)-2-hexyloxy-5-methylbenzene (**5**). This compound in a solvent mixture[11] of diethyl ether, ethanol, and 2-methylbutane (in a weight ratio of 1:1:1) formed a clear transparent glass when it was cooled to −198 °C. The absorption spectra of **5** at −198 °C (Figure 4) clearly revealed vibronic bands at 315, 331, 349, and 367 nm, which correspond to 31 746, 30 211, 28 653, and 27 248 cm^{-1}, respectively. The vibrational energy gap in the excited state of **5**, therefore, is estimated to be about 1400 cm^{-1}. It was also noted that the absorption spectrum of **5** at 25 °C exhibited a similar long tail, indicating that the long tailing observed in the absorption spectrum of **3** was an intrinsic property of the chromophore.



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The fluorescence spectrum of **3** in THF revealed a major band at 421 nm at room temperature. As the temperature was lowered to −108 °C, the vibronic bands were only partially resolved (Figure 3). Further cooling the sample to −198 °C froze the sample solution into the solid state, eliminating most of the molecular motions and increasing the spectroscopic resolution. The fluorescence spectrum at −198 °C clearly revealed several vibronic bands at 382, 405, 429, and 455 nm, which correspond to 26 178, 24 691, 23 310, and 21 978 cm^{-1}, respectively. The distribution of the viberational energy levels in the ground state of **3** fits an anharmonic oscillator model. The vibrational energy gap in the

Table 1. Comparison of Spectroscopic Data of Polymers in THF at 25, − 108, and −198 °C[a]

	polymer **3**		polymer **4**	
temperature/°C	UV−vis (λ_{max}/nm)	fluorescence (λ_{max}/nm)	UV−vis (λ_{max}/nm)	fluorescence (λ_{max}/nm)
25	307	421	**372**, ~393 (sh)	~413 (sh), **437**
−108	**314**, 355 (sh), 373 (sh)	405, **425**, 452 (sh)	360, **377**, 399	419, **444**
−198		382, 405, **429**, 455		419, **445**, 474 (sh)

[a] Bold data indicate the most intense peak.

ground state of **3** is, therefore, estimated to be about 1487 cm^{-1}. The emission band at 382 nm, which is clearly visible at −198 °C, appears at the edge of the long absorption tail, indicating that it might be attributed to the 0−0 transition. The wavenumber separation between the emission band at 382 nm (26 178 cm^{-1}) and the absorption band at ~ 373 nm (26 810 cm^{-1}) is estimated to be 632 cm^{-1}, much smaller than the required 1487 cm^{-1} for a lower energy level in the anharmonic oscillator model. Therefore, the emission bands at 382, 405, 429, and 455 nm are assigned to 0−0, 0−1, 0−2, and 0−3 transitions, respectively.

Both absorption and emission spectra of **3** (Figure 3) indicate that the 0−0 transition band is the weakest, suggesting that the molecular geometry in the excited state is quite different from that in the ground state.[12] The geometrical difference between the ground and excited states of **3** appears to be larger than that of **4**. This can be rationalized by considering the molecular structure of the chromophore in the respective polymers. The substituents in the chromophore of the block copolymer **4** are attached to the side phenyl and are oriented to point outward. Such arrangement minimizes the steric interaction between the substituents and the chromophore in **4**, permitting all three phenyls in the chromophore to maintain planarity and maximum conjugation.[13] Steric interaction of the alkoxy side chain with the olefin in **3**, however, may force the two adjacent phenyls to deviate from coplanarity.

The fluorescence spectrum of **5** exhibited a broad emission peak at about 398 nm at 25 °C (Figure 4). As the temperature was decreased to −198 °C, the broad peak was successfully resolved into several bands with λ_{max} at 371, 392, and 415 nm, which correspond to 26 954, 25 510, and 24 096 cm^{-1}, respectively. The vibrational energy gap in the ground state of **5** was estimated to be about 1444 cm^{-1}, which is comparable to the 1487 cm^{-1} separation observed in **3**. At low temperatures, the highest energy band (λ_{max} = 371 nm or 26 954 cm^{-1}) in the emission spectrum significantly overlapped the lowest energy band (λ_{max} = 367 nm or 27 248 cm^{-1}) in the absorption spectrum. The wavenumber separation between the peaks of the two overlapping bands was only about 294 cm^{-1}, which is much smaller than the required adjacent energy gap of 1444 cm^{-1} for a lower energy level in an anharmonic oscillator model. The emission bands at 371, 392, and 415 nm were, therefore, attributed to the 0−0, 0−1, and 0−2 transitions, respectively.

It should be noted that the 0−0 transition in **5** gives the most intense emission, indicating that both the ground and excited states adopts very similar molecular geometries. This is in sharp contrast with the emission profile observed from polymer **3** (Figure 3), in which the 0−2 transition gives the most intense emission at −198 °C. This can be rationalized by considering the influence of the polymer backbone on the chromophore alignment. As the temperature is lowered, the chromophore attempts to adopt a more planar conformation as indicated by observed bathochromic shift in the absorption spectrum. During the temperature change from 25 to −198 °C, the chromophore in **5** can move responsively to an equilibrium planar conformation before it is frozen in the glass state. In contrast, the motion of the chromophore in **3** is limited by the polymer backbone. As a result, the chromophore in **3** may not achieve an equilibrium conformational change before it is frozen. This assumption agrees with the low-temperature emission spectrum of polymer **4** (Figure 2), in which the 0−0 emission is almost the strongest at −198 °C. It appears that the soft block in the copolymer **4** exerts a somewhat smaller effect on chromophore alignment in comparison with the relatively rigid backbone in **3**, thereby allowing the chromophore in the former to achieve a nearly ideal planar conformation.

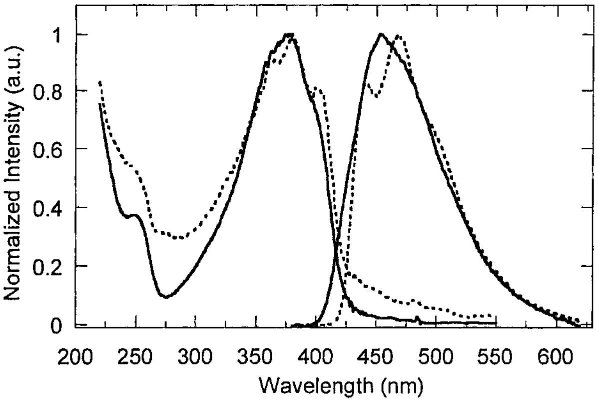

Figure 5. UV−vis and PL spectra of film **4** at 25 °C (solid line) and −198 °C (dotted line).

Thin film properties are of practical importance, as they are directly used as emission media in various optoelectronic devices. UV−vis absorption of film **4** exhibited a major band with $\lambda_{max} \approx$ 378 nm. As the temperature was lowered to −198 °C, the major absorption band became structured with observable vibronic bands at 359, 380, and ~402 nm (Figure 5). The vibronic band positions observed from the film state are essentially identical to that detected in solution at −108 °C (Table 1), confirming that the chromophore in **4** remains well isolated in the solid state. Emission of the film **4** at room temperature shows one peak with $\lambda_{max} \approx$ 453 nm, which is clearly resolved into two bands with λ_{max} at 442 and 468 nm at −198 °C.

The UV−vis absorption of film **3** (Figure 6) exhibited an absorption profile with $\lambda_{max} \approx$ 312 nm, which closely matched that observed in the solution spectrum. A temperature decrease from 25 to −198 °C caused essentially no change in the absorption spectrum, as the tight packing in the solid state allows only limited molecular motion. In contrast to film **4**, the emission spectrum of film **3** showed some vibronic structure at room temperature, which may be attributed to a more rigid environment in the film state than in the solution state. The vibrational structure of film **3** became more

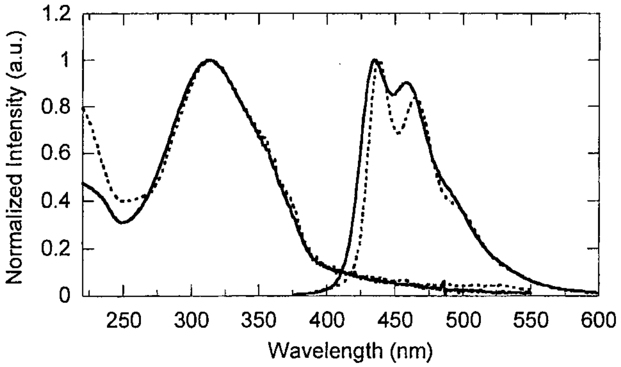

Figure 6. UV−vis and PL spectra of film **3** at 25 °C (solid line) and −198 °C (dotted line).

pronounced at −198 °C, apparently due to the reduced molecular vibration at low temperature. The emission bands (λ_{max} = 435 and 459 nm) at 25 °C were also slightly red-shifted to λ_{max} = 438 and 465 nm, indicating that the chromophore in the film state is still responsive to temperature change.

Conclusion

Optical properties of blue-emitting poly(*m*-phenylenevinylene) **3** are very similar to that of the model compound **5** as a result of π-conjugation interruption at *m*-phenylene. UV−vis and fluorescence spectra at low temperature have successfully resolved the hidden vibronic structures in **3**, **4**, and **5**, thereby leading to the assignment of vibrational transitions. Emission spectra of both blue-emitting polymers **3** and **4** reveal a similar distribution of vibrational energy levels, which are characteristic for an anharmonic oscillator. The vibrational energy level of **3** (1487 cm^{-1}) is slightly larger than that of PPV block copolymer **4** (1394 cm^{-1}) in the solution emission spectra. The chromophore in the poly(*m*-phenylenevinylene) **3** consists of a 1.5 phenylenevinylene unit, while that in the PPV block copolymer **4** a 2.5 phenylenevinylene unit. Although the UV−vis absorption λ_{max} of **3** (307 nm) is quite different from that of **4** (372 nm), their emission λ_{max} values are very similar (421 nm for the former and 437 nm for the latter). While the presence of the unsaturated substitution on the chromophore in **3** at the meta position increases its conjugation length, the predominant emission from 0−1 and 0−2 transitions (not 0−0 transition) in **3** also contribute to the red-shifted emission.

Experimental Section

Materials and Instrumentation. Polymers **3**[9] and **4**[7a] and the model compound **5**[9] were prepared as reported previously. UV/vis spectra were recorded either in distilled dry tetrahydrofuran (THF) or from films spin-cast on quartz tubes on a Hewlett-Packard 8543 diode array spectrophotometer. Fluorescence spectra were recorded on a PTI steady-state fluorometer. The optical spectra at −108 °C were measured by using the conditions[8] reported previously. For the spectra at −198 °C, the sample solution in a 5 mm quartz NMR tube was immersed in liquid nitrogen.

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(13) Molecular mechanics calculation shows that the dihedral angle between the end and central phenyl is about 0.4° for the chromophore in **4.** The dihedral angle between the two phenyl in the chromophore of **3** is ~7.7°. The molecular modeling was performed by using HyperChem version 6.03.

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