



A study of vibronic structures in the optical spectra of oligo(thienylene ethynylene)s

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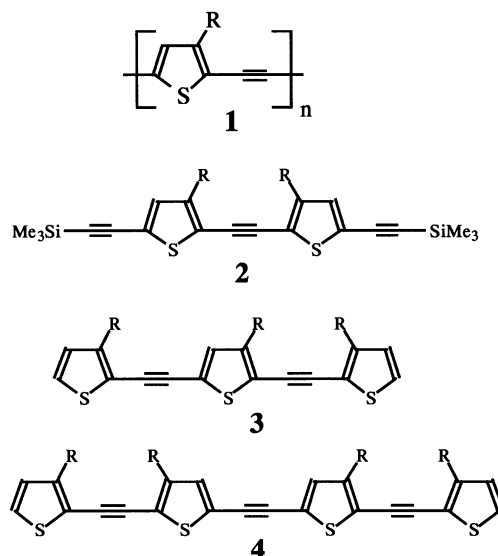
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Abstract—At the low temperature, hidden vibronic structures were successfully resolved in the absorption spectra of oligo(thienylene ethynylene)s **2–4**. Identification of the lowest energy absorption band aids the assignments of the vibronic structures in these molecules. The emission λ_{max} values were also found to be slightly red-shifted at the low temperature, indicating the adoption of a more planar conformation. The temperature-induced change in molecular conformation appeared to be dependent on the conjugation length of the molecules. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Poly(thienylene ethynylene)s (PTEs, **1**), where the substitute R at the β -position may be an alkyl or aryl, are a class of π -conjugated materials with interesting electrical and optical properties. For example, oligomers of PTE with defined chain length show potential applications¹ as ‘molecular wires’. The optical absorbance¹ of poly(3-ethylthienylene ethynylene) increases with chain length, reaching an optical saturation at about 440 nm.^{2,3} Photoluminescence (PL) of the polymer⁴ in solution exhibits two bands. Although the emission maxima of both high- and low-energy bands increase with the chain length, the relative intensity of the low-energy band gradually decreases with the chain length. Further study is desired to elucidate the emission characteristics and its dependence on the chain length, which is of fundamental importance in understanding the optical properties of these materials. Since examination of well-defined oligomers⁵ will provide intuitive knowledge about the electronic and optical properties of the π -conjugated polymer backbone, we have studied the fluorescence vibronic structures of oligo(thienylene ethynylene)s **2–4**, and report our results herein.



2. Results and discussion

It is known that temperature plays an important role in the detection of structured emission, since a vibrational structure becomes increasingly prominent at low temperature.⁶ Thus, the solutions of oligomers⁷ **2–4** in THF were cooled to -108°C by gradually pouring liquid nitrogen into the sample solutions while they remained clear. Bis[3-hexyl-5-[(trimethylsilyl)ethynyl]-2-thienyl]ethyne (**2**) exhibited some vibronic structures in both

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absorption and fluorescence spectra at room temperature (Fig. 1). These vibronic structures became more pronounced at -108°C , attributed to the reduced rotation and increased solvent viscosity at the low temperature. At the low temperature, the absorption and emission λ_{max} values were slightly red-shifted ~ 2 nm (Table 1) relative to their respective room temperature spectra.

The emission spectrum of **2** at -108°C showed two well-resolved bands at 410 and 431 nm, and shoulders at ~ 450 and ~ 475 nm, which correspond to the wavenumbers of 24390, 23202, 22222, and 21053 cm^{-1} , respectively. The vibrational energy levels of **2** in the ground state (as shown from the emission spectrum) appeared to be about equally spaced with a wavenumber separation of about 1188 cm^{-1} , or a wavelength separation of about 21 nm, which was expected from the theoretical model⁸ of an Anharmonic Oscillator. As observed from the low temperature spectra of **2** (Fig. 1), the lowest energy band ($\lambda_{\text{max}} = 399$ nm) in the absorption spectrum would significantly overlap with the highest energy band ($\lambda_{\text{max}} = 410$ nm) in the emission spectrum. The wavenumber separa-

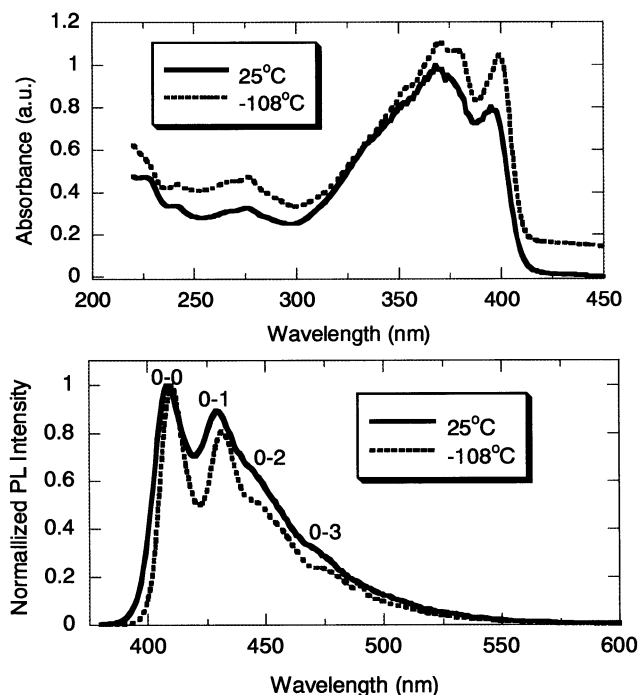


Figure 1. UV-vis (top) and fluorescence (bottom) spectra of **2** in THF at 25 and -108°C . The spectra were normalized for comparison. The absorption spectra were slightly offset for clarity.

Table 1. Comparison of spectroscopic data at room (25°C) and low (-108°C) temperature

Oligomers		2	3	4
UV-vis λ_{max} (nm)	25°C	368 , 395	370 , ~ 400 (sh)	268, 396
	-108°C	370 , 379, 399	374 , ~ 400 (sh)	269, 405
Fluorescence λ_{max} (nm)	25°C	408 , 429	413 , 436	450 , 479
	-108°C	410 , 431	416 , 439	455, 484

Bold character indicates the most intense peak.

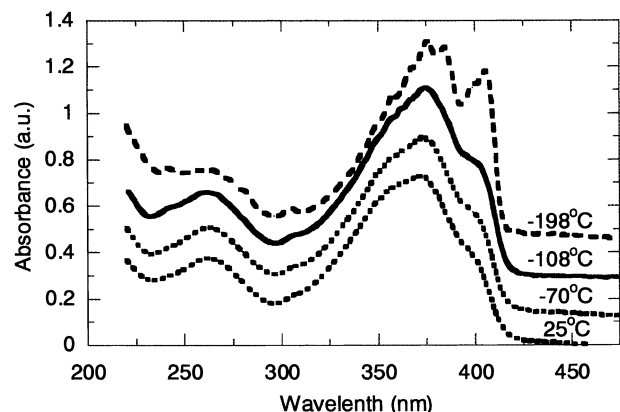


Figure 2. UV-vis spectra of **3** in THF at 25, -70 , and -108°C . The spectrum at -198°C was recorded at a glass state formed from a solvent mixture of diethyl ether, ethanol, and 2-methylbutane ($\lambda_{\text{max}} = 376$, 386, and 405 nm). The spectra were offset for clarity.

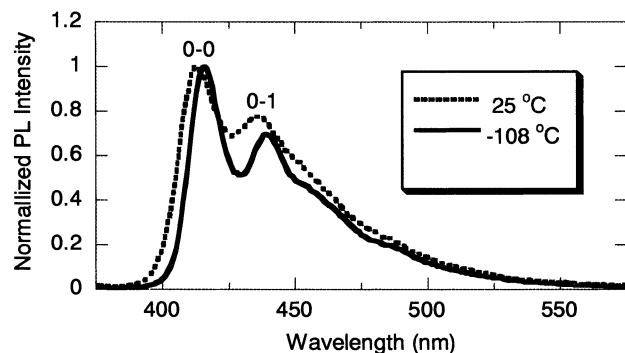


Figure 3. Photoluminescence spectra of **3** in THF at 25°C , -108°C .

tion between the peaks of the two overlapping bands at 399 nm (the absorption band, 25063 cm^{-1}) and at 410 nm (the emission band, 24390 cm^{-1}) was estimated to be 673 cm^{-1} , which is much smaller than the required adjacent energy gap of at least 1188 cm^{-1} for a lower energy level in an Anharmonic Oscillator model. Therefore, the emission bands at 410, 431, 450, and 475 nm were assigned to 0–0, 0–1, 0–2, and 0–3 transitions, respectively. In addition, the emission intensity ratio of the 0–0 to 0–1 transitions was slightly increased at -108°C (in comparison with that at 25°C). The increased emission from the 0–0 transition of **2** was apparently related to its increased absorbance for the lowest energy absorption band (399 nm, 0'–0' band) at the low temperature.

UV-vis spectra of 2,5-bis[3'-hexyl-2'-thienyl]ethynyl]-3-hexylthiophene **3** were recorded in THF at 25, -70, and -108°C (Fig. 2). As the temperature lowered, the shoulder at ~400 nm became more pronounced. To further resolve the hidden band, the sample in a solvent mixture⁹ of diethyl ether, ethanol, and 2-methylbutane was cooled down to -198°C in the liquid nitrogen to form a clear transparent glass. The absorption spectrum at -198°C (Fig. 2) exhibited clearly resolved bands with absorption $\lambda_{\text{max}} = 376, 386,$ and 405 nm, which confirmed the presence of the absorption band at ~400 nm.

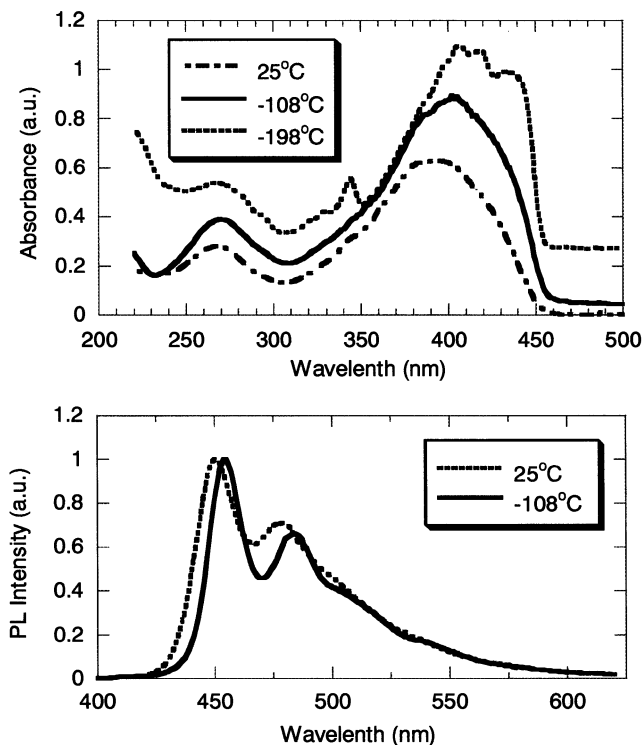


Figure 4. UV-vis (top) and fluorescence (bottom) spectra of **4** in THF at 25 and -108°C. The UV-vis spectra were offset for clarity.

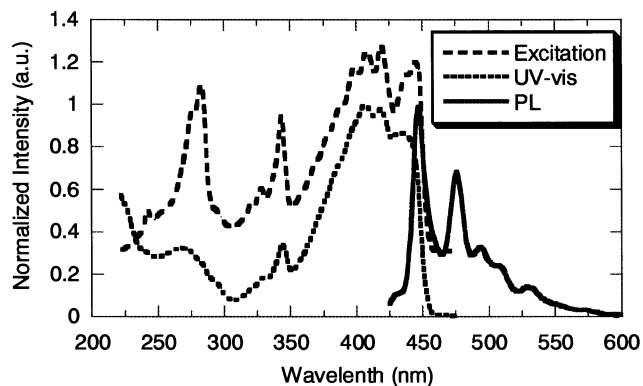


Figure 5. UV-vis, excitation, and fluorescence spectra of **4** in the solvent mixture of diethyl ether, ethanol, and 2-methylbutane at -198°C.

Photoluminescence spectra of **3** were recorded in THF solvent at 25 and -108°C (Fig. 3). The spectrum at -108°C was red-shifted ~3 nm relative to that at 25°C, with the emission λ_{max} at 416 and 439 nm (corresponding to the wavenumber of 24038 and 22779 cm^{-1} , respectively). The vibrational energy levels of **3**, therefore, appeared to be separated by a wavenumber of about 1259 cm^{-1} or a wavelength separation of about 23 nm. In other words, an energy gap of at least 1259 cm^{-1} was required for a lower vibrational energy level to occur in an Anharmonic Oscillator model. The wavenumber separation between the low-energy absorption band at ~400 nm (~25000 cm^{-1}) and the high-energy emission band at 416 nm (24038 cm^{-1}) was estimated to be only 962 cm^{-1} (smaller than the required 1259 cm^{-1}). Therefore, the emission bands of **3** at about 416 and 439 nm were assigned to 0-0 and 0-1 transitions, respectively.

UV-vis spectra of **4** (Fig. 4) at 25 and -108°C did not reveal any visible vibronic structures for the major absorption band at about 400 nm, although the absorption λ_{max} for the spectrum at the low temperature was slightly red-shifted (~6 nm). It appeared that the absorption band became more and more difficult to resolve as the conjugation length of the oligomer increased. A glass solid of **4** was prepared from the solvent mixture of diethyl ether, ethanol, and 2-methylbutane at -198°C. The broad absorption peak at about 400 nm was resolved into a few bands at -198°C (Fig. 4) with absorption λ_{max} values of 407, 418, and 434 nm. The observed new band at about 434 nm was not due to the possible formation of a chromophore aggregation, since the onset of the absorption spectra did not change with the temperature.¹⁰ The minor peak at ~344 nm was also a result of the low temperature effect, as it was not observed at 25°C. Excitation spectrum (Fig. 5) also revealed very similar vibronic structure (Fig. 5) with the lowest energy band exhibited at 445 nm, which was slightly red-shifted in comparison with that at 434 nm observed from its absorption spectrum.

Photoluminescence of **4** revealed structured emission at 25 and -108°C (Fig. 4). By using the fluorescence data at -108°C, the wavenumber separation between the emission bands at 455 nm (21978 cm^{-1}) and 484 nm (20661 cm^{-1}) was estimated to be about 1317 cm^{-1} (corresponding to a wavelength separation of about 29 nm). The wavenumber separation between the high energy emission band at 455 nm and the low energy UV-vis absorption band at ~434 nm (23041 cm^{-1}) was estimated to be 1063 cm^{-1} , which is smaller than the required adjacent vibrational energy gap of at least 1317 cm^{-1} for a lower energy level. Therefore, it was likely that the emission bands at 455 and 484 nm were from the 0-0 and 0-1 transitions, respectively. This assignment was further confirmed by direct comparison between the absorption and fluorescence spectra of the transparent glass formed from the solvent mixture (diethyl ether, ethanol, and 2-methylbutane) at -198°C (Fig. 5). Emission bands from the frozen transparent glass exhibited two major bands with emission λ_{max} at 447 and 476 nm, which is slightly blue-shifted (~3 nm) in comparison with that observed in THF solvent.

Photoluminescence spectrum of **4** in THF at -108°C was red-shifted about 5 nm relative to that at 25°C . As seen from Table 1, this bathochromic shift observed in THF was gradually increased with the conjugation length of the oligomer (~ 2 nm for **2**, ~ 3 nm for **3**, and ~ 5 nm for **4**) when the temperature was lowered from 25 to -108°C . Emission at the low temperature would typically occur from the Frank–Condon state, which is the nonrelaxed state and permit a clearer correlation of fluorescence with the molecular structures. Since the mobility of the solvent was reduced at the low temperature, a blue shift in the emission was usually expected from the Frank–Condon state,^{11,12} which had a higher energy than the solvent relaxed state. In addition, the molecules in solution were considered to be isolated (no aggregation was observed) at both 25 and -108°C , and the optical spectra would provide useful information about the molecular conformation. The observed red-shifted emission spectra from **2** to **4** at low temperature, therefore, suggested that the molecules might adopt a more planar conformation at the low temperature than that at room temperature. This temperature-induced conjugation length change in oligo(thienylene ethynylene)s **2–4** appeared to be smaller than that observed from the 1,4-distyrylbenzene derivative, which exhibited about an 8–9 nm bathochromic shift¹³ in the emission spectra when the temperature was changed from 25 to -108°C .

Acknowledgements

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References

1. Pearson, D. J.; Schumm, J. S.; Tour, J. M. *Macromolecules* **1994**, *27*, 2348–2350.
2. Schumm, J. S.; Pearson, D. L.; Tour, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33* (13), 1360–1363.
3. Tour, J. M. *Chem. Rev.* **1996**, *96*, 537–553.
4. Li, J.; Pang, Y. *Macromolecules* **1997**, *30*, 7487–7492.
5. Wegner, G.; Müllen, K. *Electronic Materials: The Oligomer Approach*; Wiley-VCH: Weinheim, 1997.
6. (a) Perkampos, H.-H. *UV-vis Spectroscopy and Its Applications*; Springer-Verlag: Berlin, 1992; Chapter 8; (b) Downs, A. J. *Low Temperature Molecular Spectroscopy*, NATO ASI Ser. C; Kluwer Academic, Dordrecht: 1996; Vol. 483, Chapter 1.
7. Oligomers **2–4** were prepared as reported previously.⁴ The temperature from 25 to -100°C was directly measured by using a low temperature thermometer before and after the measurement ($\pm 0.2^{\circ}\text{C}$). The temperature of -108°C was conveniently determined by observing the THF solid-solution equilibrium (mp of THF solvent was -108°C).
8. Turro, N. J. *Modern Molecular Photochemistry*; University Science: Mill Valley, 1991; Chapter 4.
9. Schäfer, E. P. *Dye Lasers*, 3rd ed.; Springer-Verlag: Berlin, 1990; p. 18.
10. Rughoputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J. Polym. Sci.: Part B: Polym. Phys.* **1987**, *25*, 1071–1078.
11. Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 2nd ed.; Kluwer Academic: New York, 1999; p. 198.
12. Hercules, D. M.; Rogers, L. B. *J. Phys. Chem.* **1960**, *64*, 397–400.
13. Liao, L.; Pang, Y. *J. Mater. Chem.* **2001**, *11*(12), 3078–3081.