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A study on the vibrational structure of poly(phenylenevinylene)s *via* low-temperature UV-vis and fluorescence spectroscopy

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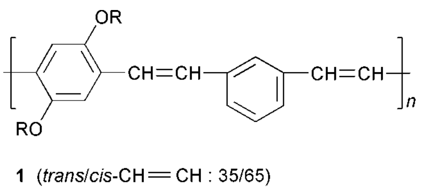
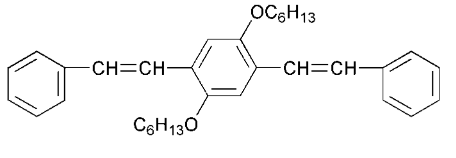
UV-vis and fluorescence spectroscopy of poly(phenylenevinylene) derivatives were acquired at low temperature (−108 °C). Noticeable spectroscopic red-shifts (as large as 17 nm) were detected from both polymers and model compounds in solutions when the temperature was decreased from 25 °C to −108 °C, indicating that the molecules adopted a more planar conformation at the low temperature. The low temperature spectra revealed the hidden structured absorption and emission. The vibrational structures in the fluorescence spectra were analyzed by using the obtained spectroscopic data at the low temperature. The very similar spectroscopic properties between the polymers (**1** and **2**) and their model compounds (**3** and **4**) strongly suggested that the observed spectroscopic red-shift from the polymers at the low temperature was an intrinsic property of the chromophore.

Introduction

Use of fluorescent π-conjugated polymers in emerging technologies, such as LED displays,[1] sensors[2] and lasers,[3] is rapidly expanding since the first demonstration of a polymeric LED device.[4] Detailed study on the optical properties of these materials will allow us to gain a comprehensive understanding, thereby assisting the development and application of new materials in the future. Recent studies[5] on poly[(*m*-phenylenevinylene)-*alt*-(1,4-dialkoxy-2,5-phenylenevinylene)] derivatives **1** and **2** show that they are highly luminescent materials with improved solubility. Comparison of the absorption and emission spectra between polymer **2** and its model compound **4** indicates that they have a strikingly similar electronic band structure,[5a] as a result of effective "through conjugation" interruption at *m*-phenylene units. To evaluate the effect of the olefin bond geometry on the properties of the polymers, isomers **1** and **2** with different ratios of *trans*/*cis*-CH=CH have been synthesized to compare with the model compound pair **3** and **4**.



1 (*trans*/*cis*-CH=CH : 35/65)
2 (*trans*/*cis*-CH=CH : 93/7)
(**a**, R = *n*-hexyl; **b**, R = *n*-butyl)



3 (*trans*/*cis*-CH=CH : 41/59)
4 (*trans*/*cis*-CH=CH : 99/1)

Although the absorption λ_{max} value of **2** (404 nm) was noticeably different from that of **1** ($\lambda_{max} = 394$ nm), their photoluminescence (PL)[5] is almost identical. The same trend was also observed when comparing the model compound pair **3** and **4** (Fig. 1). It appears that there was a large difference (Stokes shift) in λ_{max} values between the absorption band of the lowest energy and the emission band of the highest energy ($\sim$60 nm for **1b**, $\sim$41 nm for **2b**, and $\sim$51 nm for **3** and **4**). In addition, the absorption $\lambda_{max} \approx 390$ nm is falling out of, while the emission maximum $\lambda_{max} \approx 440$ nm is at the edge of, the overlapping region between the absorption and emission spectra (Fig. 1). This raises a question whether the most intense emission band originates from the 0–0 transition, as it is a common transition[6] used for both optical absorption and emission processes. Since the assignment of the vibrational structure is of fundamental importance in understanding the optical properties of these fluorescent π-conjugated polymers, and in establishing the valuable structure–property correlation, we have carried out a low temperature spectroscopic study on these materials and report the results herein.

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 temperatures.[7] To

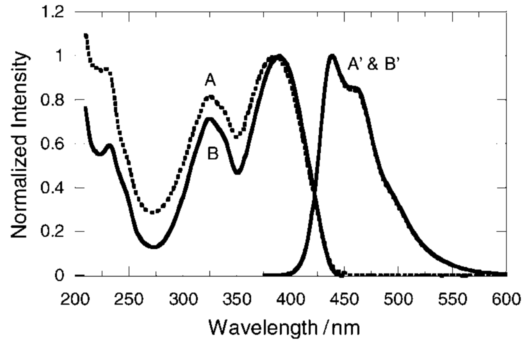


Fig. 1 UV-vis (A and B) and PL (A′ and B′) spectra of **3** and **4** respectively in THF solution at room temperature. The spectra are normalized for comparison (by using the absorption peak at about 390 nm for curves A and B, and the emission peak at 439 nm for curves A′ and B′).

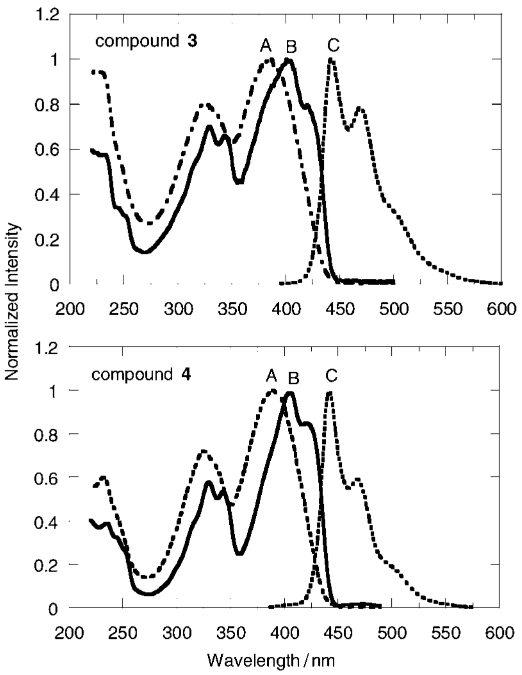


Fig. 2 UV-vis spectra of **3** (top) and **4** (bottom) at 25 °C (curve A) and −108 °C (curve B), and fluorescence spectrum at −108 °C (curve C).

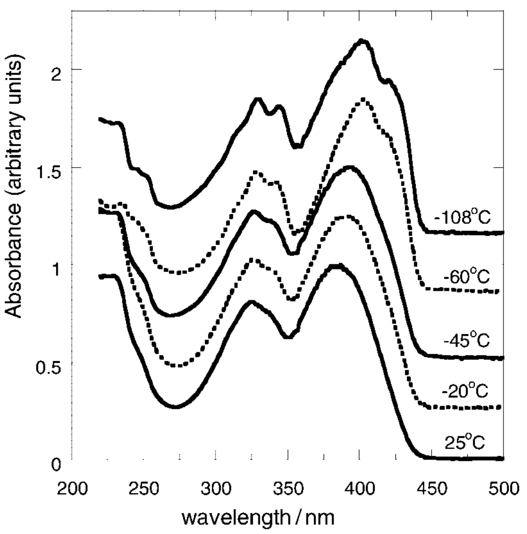


Fig. 3 UV-vis absorption spectra of **3** in THF at various temperatures. The spectra are offset for clarity.

examine the temperature effect on the emission characteristics of **3** and **4**, the sample solutions in THF were cooled to −108 °C by gradually pouring liquid nitrogen into the sample solutions while they remained clear. The spectra acquired at the low temperature (−108 °C) are shown in Fig. 2. In addition to the increased intensity at the low temperature, the shoulders at ~460 nm in the room temperature spectrum (Fig. 1, curves A′ and B′) were clearly resolved into a pronounced peak, attributed to the reduced rotation and increased solvent viscosity at the low temperature. The low-temperature emission spectra were also slightly red-shifted with the emission λ_{max} at 443 nm and 469 nm (~4 nm red-shifted). Further cooling to −195 °C (liquid nitrogen temperature) froze the sample solution, but did not cause additional red-shift in the emission λ_{max} values. Emission at the low temperature typically occurs from the Frank–Condon state,[8] which is the non-relaxed excited state and permits a clearer correlation of fluorescence spectra with molecular structures. Since the mobility of the solvent was reduced at the low temperature, a blue-shift[8,9] in the emission was usually expected from a Frank–Condon state, which has a higher energy than the solvent relaxed state. The observed red-shifted emission spectra from **3** and **4** at the low temperature suggested that the molecules might adopt a more planar conformation at the low temperature than that at room temperature.

It was noted that the absorption spectra of the polymers would also respond to the molecular conformation changes at the low temperature, as a more planar molecular conformation ensures a better overlap among the conjugated p-orbitals.[10] Thus, the low temperature UV-vis spectra of **3** and **4** were acquired in THF solution (~2×10^{-5} M). As shown in Fig. 3, the absorption λ_{max} value exhibited a gradual red-shift of about 14 nm for the former and 17 nm for the latter, respectively, when the temperature was lowered from 25 °C to −108 °C (see also Table 1). In addition, the vibrational structure in the absorption bands started to appear when the temperature was decreased to about −60 °C. It appeared that lowering the temperature to −108 °C was necessary to clearly resolve the low-energy absorption band at about 387 nm. Although resolution[11] of overlapping UV-vis absorption bands was possible *via* computer-aided mathematical analysis, application of a second derivative curve on the curves A and B in Fig. 1 failed to generate any intuitive information about the hidden vibronic structure in the room temperature spectra. The observed new band in the low temperature UV-vis spectra at about 420 nm was not due to the possible formation of a chromophore aggregation, since the onset of the absorption spectra did not change with the low temperature, and the absorption profiles were not affected by the concentration. The conclusion was also supported by the absence of the emission from a chromophore aggregate, which was expected to occur at a longer wavelength with the emission intensity[12] increasing at lower temperatures.

The low-temperature emission spectrum of **3** (Fig. 2) showed two distinctive bands at 443 nm and 469 nm, and a shoulder at about 500 nm, which corresponded to the wavenumbers 22 624 cm^{-1}, 21 322 cm^{-1} and 20 000 cm^{-1}, respectively. The vibrational energy levels of **3** in the ground state (as shown from the emission spectrum) appeared to be about equally spaced with a wavenumber separation of about 1300 cm^{-1}, or a wavelength separation of about 27 nm, which is expected from the theoretical model[13] of an Anharmonic Oscillator. As displayed from the low-temperature spectra of **3** (Fig. 2), the highest energy band of the fluorescence spectrum (curve C) overlapped with the lowest energy band of the absorption spectrum (curve B) in the region of 418–443 nm. The wavenumber separation between the peaks of the two overlapping bands at 442 nm (the emission band, 22 624 cm^{-1}) and at 420 nm (the absorption band, 23 809 cm^{-1}) was estimated to

Table 1 Comparison of spectroscopic data at room (25 °C) and low (−108 °C) temperature[a]

Polymers or oligomers		**1b**	**2b**	**3**	**4**
UV-vis λ_{max}/nm	25 °C	328, **394**	328, **404**	326, **387**	324, **390**
	−108 °C	333, **409**, 433	333, 414, **435**	329, 340, **401**, 420	330, 344, **407**, 422
Fluorescence λ_{max}/nm	25 °C	**446**, 473	**445**, 473	439	439
	−108 °C	**455**, 484, 515(sh)	**453**, 482, 513(sh)	**443**, 469, 500(sh)	**442**, 468, 499(sh)

[a] The **bold** number indicates the most intense peak.

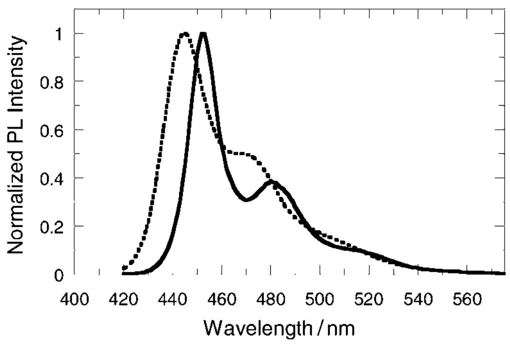


Fig. 4 Normalized PL spectra of **2b** in THF at 25 °C (dotted line) and at −108 °C (solid line).

be about 1185 cm^{-1}, which is significantly smaller than the required adjacent vibrational energy gap of at least 1300 cm^{-1} for the lower energy level in an Anharmonic Oscillator model.[13] Therefore, it was likely that the emission bands at 442 nm, 469 nm and 500 nm in the low-temperature fluorescence spectrum of **3** (curve C in Fig. 2) were corresponding to the 0–0, 0–1, and 0–2 transitions, respectively. On the basis of the same reasoning, the low temperature emission bands of **4** at 442 nm, 469 nm and 499 nm were assigned to the 0–0, 0–1 and 0–2 transitions, respectively. Although the isomer pair **3** and **4** exhibited nearly identical emission profiles at room temperature (Fig. 1), the relative intensity of the 0–1 band (at 469 nm) for **4** was significantly reduced (in comparison with that for **3**) at the low temperature. Thus, the emission ratio of the 0–0 to 0–1 band for the chromophore of different molecular geometry was quite sensitive to the temperature change.

Low temperature emission spectra of the polymer solutions were also acquired under the same experimental conditions to examine the spectroscopic similarity between the polymers and their model compounds. As shown in Fig. 4, the spectra were more clearly resolved at −108 °C than at room temperature, accompanied with decreased intensity for the emission bands at longer wavelength (at about 482 nm and 515 nm). In addition, the low temperature spectra were red-shifted by about 8 nm, which is larger than the ~4 nm bathochromic shift observed for the model compound **4**.

The UV-vis absorption spectra of the polymers also exhibited bathochromic shift when the temperature was lowered from 25 °C to −108 °C. The magnitude of the bathochromic shifts were measured to be ~15 nm for **1b** and ~10 nm for **2b** (Fig. 5 and Table 1), which is larger than that (~8 nm) observed from their emission spectra. This was in agreement with the assumption that the emitting chromophore adopted a more planar conformation at the low temperature. The emission at the low temperature would occur from the Frank–Condon state,[8] which had a higher energy than the solvent relaxed state. The emission at the low temperature was, therefore, usually accompanied with a small blue-shift, which would partially offset the red-shift from the formation of a more planar molecular conformation, and thereby leading to a smaller red-shift in the emission than that in the absorption. The observed bathochromic shifts (10–15 nm) from the absorption spectra of the polymers were comparable with those from the model compounds **3** and **4** (14–17 nm). This result indicated that lowering the temperature from 25 °C to −108 °C caused a similar degree of conformation change for the chromophores in both the polymers and model compounds. The very similar spectroscopic properties between the polymers (**1** and **2**) and their model compounds (**3** and **4**), therefore, strongly suggested that the observed spectroscopic red-shift from the polymers at the low temperature was an intrinsic property of the chromophore, and was caused by the molecule conformation change.

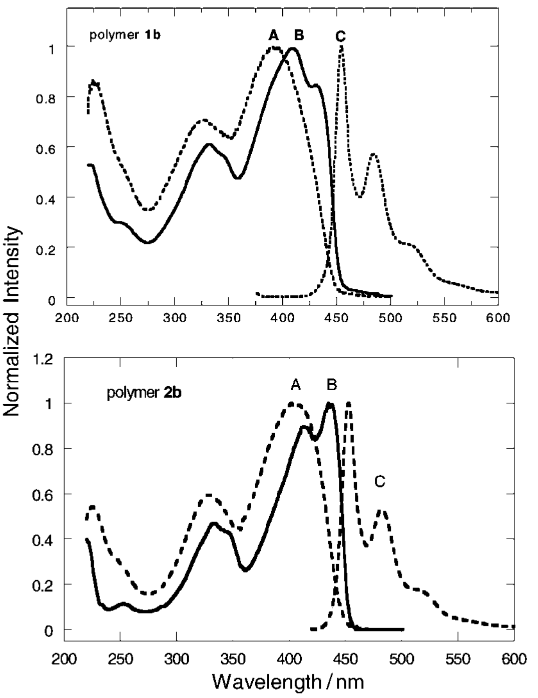


Fig. 5 UV-vis spectra of **1b** (top) and **2b** (bottom) at 25 °C (curve A) and −108 °C (curve B), and fluorescence spectra at −108 °C (curve C).

As shown in Fig. 5, the absorption band of **2b** near 404 nm at room temperature was resolved into two peaks (near 414 nm and 435 nm, respectively) at −108 °C. The newly resolved absorption peak at $\lambda_{\max} = 435$ nm was located at nearly the same position as that of **1b** (at 433 nm), although with different intensity. The presence of this common absorption band (lowest in energy) at ~433 nm in **1b** and **2b** could be responsible for their very similar fluorescence. In addition, the newly resolved absorption peak at $\lambda_{\max} = 435$ nm was within the overlapping region (430–460 nm) between the absorption (curve B) and emission (curve C) spectra of **2b** (Fig. 5). The low-temperature emission spectrum of **2b** showed two distinctive emission bands at 453 nm and 482 nm, and a shoulder at about 513 nm, which corresponded to the wavenumbers of 22 075 cm^{-1}, 20 747 cm^{-1} and 19 493 cm^{-1}, respectively. The vibrational energy levels of **2b** in the ground state were separated by a wavenumber of ~1300 cm^{-1} (or a wavelength separation of ~30 nm), which was significantly larger than the wavenumber separation (~913 cm^{-1}) between the emission maximum $\lambda_{\max} = 453$ nm (22 075 cm^{-1}) and absorption maximum $\lambda_{\max} = 435$ nm (22 988 cm^{-1}). On the basis of the same reasoning for **3** and **4**, the emission bands at 453 nm, 482 nm and 513 nm in the low-temperature fluorescence spectrum of **2b** were assigned to be 0–0, 0–1, and 0–2 transitions, respectively. The fluorescence spectra of the polymers (Fig. 5) also revealed a characteristic pattern, in which the short-wavelength vibrational band (0–0 transition) was the most intense emission, and the intensity of the emission bands gradually decreased with increasing wavelength. These characteristics suggested that the geometry of the chromophore in the excited state was very similar to that of its ground state, based on the Frank–Condon principle.[7a]

Experimental section

Materials and instrumentation

Poly[(2,5-dibutoxy-1,4-phenylenevinylene)-*alt*-(1,3-phenylenevinylene)] **1** and **2**, and 1,4-distyryl-2,5-dihexyloxybenzene **3** and **4** were prepared as reported previously.[5] The content of *trans*-CH=CH in the samples was estimated from ^{1}H-NMR on a Bruker ARX400 spectrometer. The solutions were freshly prepared by dissolving the samples in distilled dry THF solvent. UV-vis spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer. Fluorescence spectra were recorded on a PTI (Photon Technology International) steady state fluorometer. A low-temperature sample holder with a Dewar vessel was used for the measurement of the low-temperature spectra. In a typical experiment, liquid nitrogen was gradually added to the sample solution. The temperature from 25 °C to −100 °C was directly measured by using a low temperature thermometer before and after the spectrum measurement (±0.2 °C). The temperature of −108 °C was conveniently determined by observing the THF solid–solution equilibrium (mp of THF solvent is −108 °C).

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