Vibrational Structure of Organic Semiconductors: The Role of Conjugation Length

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Site-selective luminescence spectroscopy (SSL) was employed to resolve the vibracional modes in self-assembled poly(p-phenylene vinylene), PPV. Using Franck-Condon analysis, the PPV spectra can be well described by three effective vibrational modes at 330, 1160 and 1550 cm^{-1}. As the temperature increases from 4 to 180 K the electron-phonon coupling (S factor) remains constant for the 1550 cm^{-1} mode while for other lower energy modes the coupling increases monotonically. This trend is consistent with the decrease of the conjugation length due to the increase of thermal disorder. We find that the temperature dependence of vibrational progression in PPV films is determined mainly by low frequency torsional modes.

1 Introduction

The coupling of the electronic properties to structural changes is of special importance in the case of conjugated polymers [1-3]. The parameter that makes optical properties to be very sensitive to conformational and thermal disorder is the Huang-Rhys factor S. The coupling constant S is related to disorder through the degree of the chain conjugation. However, the exact relation between S-factor and conjugation length is not well establish [3]. In the present work, we studied experimentally and theoretically the effects of thermal disorder on electron-phonon coupling in the emission spectra of the model polymer poly(p-phenylene vinylene), PPV.

2 Experimental procedure

The experiments were performed with high quality PPV films prepared by self-assembly (SA) methodology and converted at 110 ^{o}C for 30 min [5]. Site-selective luminescence (SSL) was carried out using a very narrow excitation-line (spectral bandwidth of $\sim$ 1 nm), which was obtained through the dispersion of the light of a 450 W Xe-lamp by a 1 m monochromator. Details of the PL set-up are given in Ref. [5].

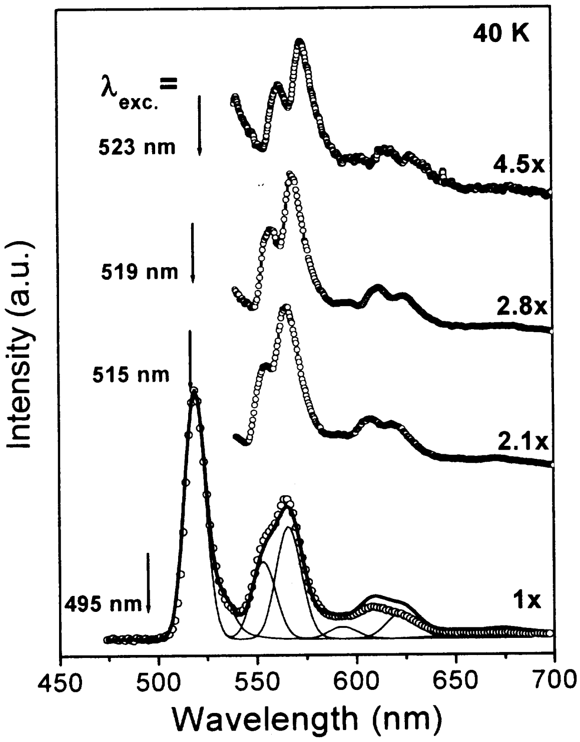

Figure 1. Dependence of SSL spectra on λ_{exc} (arrows). The bottom spectrum shows a full spectral line shape (circle) and its theoretical fit through Frank-Condon analysis (line).

3 Results and discussions

Figure 1 displays luminescence spectra (40 K) of a SA PPV film upon scanning the light excitation wavelength λ_{exc} across the low energy tail of the absorption band that overlaps the luminescence spectrum. In the non-resonant case (λ_{exc}=495 nm) we observed the standard PPV spectra with a narrow zero-phonon line at 521 nm followed by a vibronic progression consisting of least three overtones, which are the combination of different effective backbone stretching modes [3].Once λ_{exc} moves into resonance with the zero-phonon line (from 515 to 523 nm), only long (low energy) conjugated segments are excited and line narrowing occurs. As a consequence, the dominant unresolved vibronic band around 576 nm splits into a doublet. Using Franck-Condon analysis [3] for the bottom spectrum of Fig.1, we notice that the vibronic progression can be well described (continuous curve) by the overlapping of three effective, inhomogeneous broadened phonon modes with energies 330, 1160 and 1550 cm^{-1}. The last two modes coincide with the splitted structure observed in the resonant case and are assigned to stretching vibration of vinyl group and phenyl ring [3,4]. The feature around 330 cm^{-1} has been associated to low frequency out-of-plane torsional modes [4].

We used the well-resolved vibronic modes and Franck-Condon analysis to study the dependence of electron-phonon coupling on the thermal disorder. Fig. 2a shows the SSL spectra (λ_{exc}=523 nm) in the region of vibronic progressions for different temperatures varying from 40 to 120 K. In this temperature range there are no significant spectral shift and line broadening. This is of particular importance in the next analysis since the only varying parameters used in the spectral fitting were the Huang-Rhys factors S_i (i=1,2,3), i.e., the coupling constants for the modes with energies 330, 1160 and 1550 cm^{-1}, respectively. The decrease of the spectral intensity is related to non-radiactive processes activated by temperature and it was not essential in the present analysis.

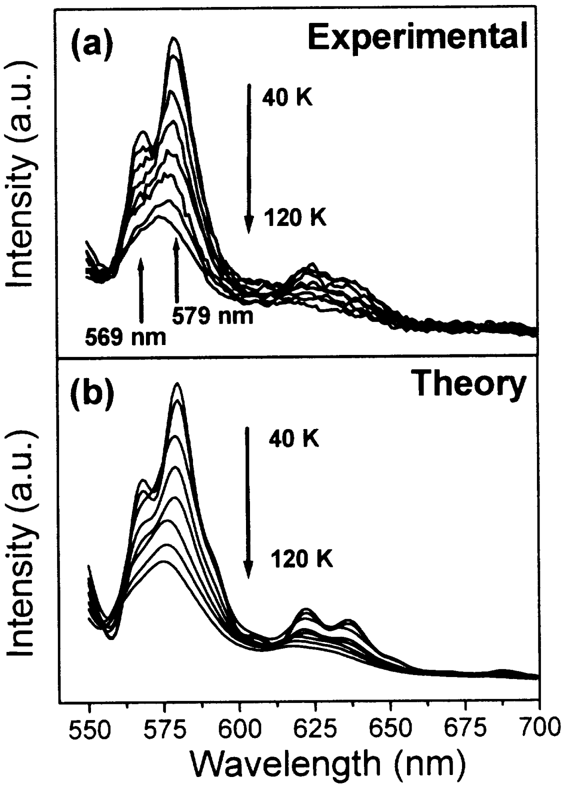

Figure 2. Temperature dependence of SSL spectra in the region of vibronic progression (a) and their theoretical fitting using Frank-Condon analysis (b).

Figure 2b shows the theoretical spectra obtained from a fit of those in Fig. 2a. The result thus calculated fits the experimental data quite well. It has to be remarked that the strong changes in the spectral shape observed in such narrow temperature range can be mainly accounted for the change of the electron-phonon coupling given by the S_i factors. The temperature dependence of each S_i obtained from the fitting is displayed in Fig. 3. One observes that the coupling constant increases with temperature for the two less energetic modes (330 and 1160 cm^{-1}). This trend is consistent with the fact that S_j is a decreasing function of conjugation length n. Since disorder decreases n, one expects that the higher the thermal disorder of a system, the larger the S factor. Conversely, the higher energy mode (1160 cm^{-1}) presented an almost constant behaviour in the temperature range. Both behaviour can be well explained by a n-dependent S_i relation of the form $S_i = S_{i0} + a_i/(n+1)$ [3], S_{i0} is the S-factor at T=0 K and a_i is an adjustable parameter. The temperature dependence of the conjugation length is given by $n = n_o \exp(-\varepsilon/kT)$ [1], where ε is a characteristic energy of the conformational process and n_o is the effective conjugation length at t=0 K. The value n_o=7 was determined from temperature dependence of the energy difference between HOMO-LUMO states. From the data of Fig. 3 one find same value of ε (=39 meV) for all phonon modes, which is in the range of the torsional barrier for polyenes [2].

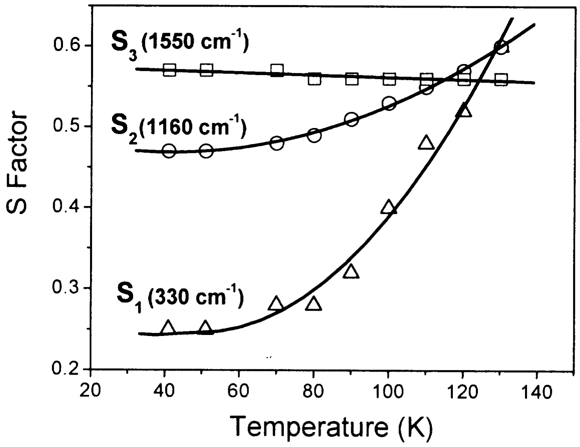

Figure 3. Temperature dependence of the S_i (i=1,2,3) factor for the effective vibrational modes (300, 1160 and 1550 cm^{-1}). The continuous lines depict the expected theoretical behaviors for each S_i.

4 Conclusion

In the present work we find that the Huang-Rhys factor of each mode increases differently with the temperature. We can regard as a result that the main changes of the luminescence spectra with temperature is accounted mainly for the variation of the electron-phonon coupling of the low frequency torsional modes.

Acknowledgement

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