Temperature effect on the electronic spectra of poly(*p*-phenylenevinylene)

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Abstract

The experimental temperature-dependent absorption, photoluminescence and photoluminescence excitation spectra of poly(*p*-phenylenevinylene) (PPV) are presented and a molecular theory is used to analyze the results. In order to model the complicated system such as PPV, the structural inhomogeneity has to be included. The structural inhomogeneity is represented by the different Huang–Rhys factors associated with different chain lengths. The theoretical spectra agree qualitatively with the experimental results.

Keywords: Poly(*p*-phenylenevinylene); Electronic spectra; Temperature effect

1. Introduction

Considerable attention has been given recently to the polymeric system of poly(*p*-phenylenevinylene) (PPV) due to its potential applications in photoelectronic devices and to its interesting structural–electronic properties. Spectroscopic experiments have been carried out in detail trying to elucidate its intricate nature, which depends not only on the synthetic methods used but also on the mechanical processes applied. Absorption, photoluminescence (PL) and photoluminescence excitation (PLE) [1–8] have been applied to the study of its optical properties. Infrared, Raman and resonant Raman techniques were used to analyze the ground state vibrational modes of PPV [4,9–14], and detailed structural information has been obtained by comparison with the theoretical calculations on oligomers [11,12]. The dynamics of excited species have been investigated by various PL [15,16] and photoinduced absorption (PA) methods [17–20] and were attributed to the formation of triplet excitons, polarons and interchain excitons. The main purpose of all these investigations is to characterize the properties of PPV systems, such as their structural content, and ground and excited electronic structures. From these results microscopic and phenomenological models can be set up, in the hope that through these models we can derive a better understanding of PPV.

Single-particle electron–hole theories, employing Hamiltonians in second quantized form, notably the SSH and SSH-like models [21–25], have been used to study the properties of solitons, polarons and bipolarons of π conjugated systems such as polyacetylene and PPV. Electronic band calculations using the valence effective Hamiltonian have been utilized to locate the bandgap energies of PPV and PPV copolymers in the hope that better material can be designed through the knowledge of relating bandgap shift to PPV backbones with different side chains [26,27].

Recently, semi-empirical molecular orbital theories have been used to study the electronic properties of PPV oligomers because, firstly, the electron–electron correlation, which is not considered in the SSH models, can be readily included through configuration interaction (CI) calculations and, secondly, higher excited state positions, both singlet and triplet, can be obtained [28–30]. Using the results of molecular orbital calculations, electronic spectra can be constructed [31,32] and a better understanding of PPV can be achieved through careful extrapolation.

Experimental studies on PPV have provided a wealth of information. Due to the polymeric and amorphous nature of such a system, not surprisingly, different conclusions (sometimes conflicting) have been drawn, for example, for the nature of the primary photoexcited species [17–20], exciton binding energies [20,33], and the dynamic processes after

excitation. Such inconsistency can also be seen in the theoretical development, i.e. whether band or molecular (exciton) theory, each with its success, is more suitable to describe PPV polymers. Band theories can provide information about binding energies of pseudo-particles such as solitons and polarons by calculating the energy offset of discrete single-electron energy levels from continuous bands. However, higher excited states, which correspond to the high energy absorption band in absorption spectra, are not easily obtainable from them. Electronic properties of PPV can be extracted from molecular theories, by modeling finite sized molecules, at the Hartree–Fock self-consistent field (HF-SCF) with configuration interaction (CI) level of theory. However, when CI is invoked in molecular theories, the convenient concepts such as excitons and polarons are lost and one has to view the system from the point of view of ground and excited states, i.e. one can only study the stationary properties of the system.

Kinetic models can be provided in order to overcome such deficiency in CI molecular theories. Recently we have set up a simple kinetic model to explain qualitatively the reason why PLE spectra are different from the absorption spectra of PPV [31]. In this paper, we will provide a more detailed kinetic model and, based on this model, theoretical temperature-dependent absorption, PL and PLE spectra of PPV are constructed. Some experimental temperature-dependent results were available [1,7] and our experimental results are also summarized. The paper is organized as follows. In Section 2, the molecular theory of absorption coefficient is presented. In Section 3, experimental details are discussed. In Section 4, the kinetic model is provided, and theoretical and experimental spectra are compared.

2. Theory

The temperature-dependent absorption and PLE spectra are calculated by summing the absorption coefficient of PPV oligomers which represent PPV segments with different chain lengths in polymers. In order to treat temperature effect on the absorption spectra of isolated molecules, the Boltzmann distribution, which is ignored in our previous study, has to be introduced. The molecular absorption coefficient for the electronic transition $a \rightarrow b$ is given by [34]

$$\alpha_{ab}(\omega) = \frac{4\pi^2\omega}{3ac\hbar} |\mu_{ba}|^2 \sum_{\nu} \sum_{\nu'} P_{a\nu} |\langle \Theta_{b\nu'} | \Theta_{a\nu} \rangle|^2 \delta(\omega_{b\nu',a\nu} - \omega) \quad (1)$$

where μ_{ba} denotes the electronic transition moment, $P_{a\nu}$ the Boltzmann factor, $|\langle \Theta_{b\nu'} | \Theta_{a\nu} \rangle|^2$ the Frank–Condon factor, a the factor which describes the medium effect, (ν, ν') the vibrational quantum numbers, c the speed of light and $\delta(\omega_{b\nu',a\nu} - \omega)$ the lineshape function [31]. Using the integral form of the delta function, the absorption coefficient is expressed as

$$\alpha_{ab}(\omega) = \frac{2\pi\omega}{3ac\hbar} |\mu_{ba}|^2 \int_{-\infty}^{\infty} dt \sum_{\nu} \sum_{\nu'} P_{a\nu} |\langle \Theta_{b\nu'} | \Theta_{a\nu} \rangle|^2 \times \exp(it(\omega_{b\nu',a\nu} - \omega)) \quad (2)$$

where, for harmonic oscillators, the Boltzmann distribution for a single vibrational mode is

$$P_{a\nu} = \frac{\exp\left[-\frac{\left(E_a + \left(\nu + \frac{1}{2}\right)\hbar\omega_{\nu}\right)}{kT}\right]}{\sum_{\nu} \exp\left[-\frac{\left(E_a + \left(\nu + \frac{1}{2}\right)\hbar\omega_{\nu}\right)}{kT}\right]} \quad (3)$$

where ν is the vibrational quantum number, ω_{ν} is the frequency of the vibrational mode and E_a is the ground energy of harmonic potential.

Assuming harmonic oscillator wavefunctions for Θ and displaced oscillators for the ground and excited states, the absorption coefficient of the single-mode case can be derived from Eqs. (2) and (3) as

$$\begin{aligned} \alpha_{ab}(\omega) &= \frac{2\pi\omega}{3ac\hbar} |\mu_{ba}|^2 \int_{-\infty}^{\infty} dt \exp\left\{it(\omega_{ba} - \omega) - S\left[\coth\left(\frac{\hbar\omega_{\nu}}{2kT}\right) - \operatorname{csch}\left(\frac{\hbar\omega_{\nu}}{2kT}\right) \cosh\left(it\omega_{\nu} + \frac{\hbar\omega_{\nu}}{2kT}\right)\right]\right\} \\ &= \frac{2\pi\omega}{3ac\hbar} |\mu_{ba}|^2 \int_{-\infty}^{\infty} dt \exp\{it(\omega_{ba} - \omega) - S[(1 + 2\bar{n}) - (1 + \bar{n}) \exp(it\omega_{\nu}) - \bar{n} \exp(it\omega_{\nu})]\} \end{aligned} \quad (4)$$

where

$$\bar{n} = \frac{1}{\exp\left(\frac{\hbar\omega_{\nu}}{kT}\right) - 1} \quad (5)$$

$S = (\omega_{\nu}/2\hbar) \Delta Q^2$ is the Huang–Rhys factor (coupling constant), and ΔQ is the displacement in normal coordinates between ground and excited states. For a molecular ensemble, a Gaussian distribution of ω_{ba} can be used to represent part of the inhomogeneity due to molecules in different orientation and environment:

$$g(\omega_{ba}) = \left(\frac{1}{2\pi d^2}\right)^{1/2} \exp\left[-\frac{(\omega_{ba} - \bar{\omega}_{ba})^2}{2d^2}\right] \quad (6)$$

where $\bar{\omega}_{ba}$ is the average (the PPV oligomer transition energies are used) electronic transition energy. Using this distribution, Eq. (4) can be averaged over ω_{ba} and the following expression is obtained:

$$\alpha_{ab}(\omega) = \frac{2\pi\omega}{3ac\hbar} |\mu_{ba}|^2 \int_{-\infty}^{\infty} dt \exp \left\{ it(\bar{\omega}_{ba} - \omega) - \frac{d^2 t^2}{2} \right\} - S[(1 + 2\bar{n}) - (1 + \bar{n}) \exp(it\omega_v) - \bar{n} \exp(it\omega_v)] \quad (7)$$

The absorption coefficient can be evaluated by calculating the Fourier transform of the kernel function in Eq. (7). For the emission coefficient, one can obtain a similar expression given as

$$I_{ba}(\omega) = \frac{2\pi a \omega^3}{3c\hbar} |\mu_{ba}|^2 \int_{-\infty}^{\infty} dt \exp \left\{ it(\bar{\omega}_{ba} - \omega) - \frac{d^2 t^2}{2} \right\} - S[(1 + 2\bar{n}) - (1 + \bar{n}) \exp(it\omega_v) - \bar{n} \exp(it\omega_v)] \quad (8)$$

3. Experimental

The PPV samples were prepared according to a modified Wessling procedure [35] as discussed previously [31]. However, in the present study, the samples were coated on sapphire plates instead of fused silica plates. The absorption spectra were measured with two different systems: one with a Hitachi U-3200 spectrophotometer and the other with a homemade temperature-controlled spectrometer. With the Hitachi spectrophotometer, absorbance of the samples in a wide spectral range (about 13 000–45 000 cm^{-1}) can be taken. However, limited by the physical configuration of the spectrophotometer, it is not easy to combine it with our temperature-controlling equipment. Therefore, the wide-range absorption spectra can be measured only at room temperature. The thicknesses of samples were thin judged from the absorption OD in the range of 0.96–1.1 and actual measurement was not performed.

In the homemade system, the samples were mounted, in vacuum, on the cold head of a CTI-Cryogenics model-22C Cryodyne refrigeration system. The temperature range in which the measurements were done was from 10 to 330 K. A 200 W tungsten lamp was used as the light source. The transmitted beam was collected with an optical fiber bundle connected to the entrance slit of an OSMA spectrometer. The spectrum through an uncoated sapphire plate was taken as the background, and the spectrum through the sample on the sapphire plate was taken afterward and divided by the background spectrum to obtain the absorbance spectrum. Except

for the temperature-controlling capability, the operations for these two systems are essentially the same. The drawback of the homemade system, in comparison to the Hitachi spectrophotometer, is that the spectral range measured is much narrower (about 13 000–22 000 cm^{-1}). The results for 80 and 300 K are shown in Fig. 1.

PL and PLE spectra were measured with a Hitachi F-4010 fluorescence spectrophotometer. For randomly oriented PPV thin films on sapphire plates, temperature-dependent PLE spectra can be measured by mounting the sample on the cold heads of cooling systems. A Janis VPF-100 variable temperature pourfill cryostat was used to cool the samples down to 77 K. In the PLE experiments, the spectra were measured by scanning the excitation wavelength, while monitoring the emission intensity at the luminescence region of the sample. Care must be taken to eliminate the scattered excitation light from the grating due to higher-order diffraction at the luminescence inlet of the spectrophotometer. A long-pass color glass filter (Newport GG.400) was put in the fluorescence light path for this purpose. All of the PLE spectra were taken with bandwidth 3 nm for excitation beam and 10 nm for fluorescence detection.

As is well known, there are three peaks in the PL spectra of PPV in the range of 510 to 600 nm [1,2] and our PL spectra for 300 and 77 K are shown in Fig. 2. The exact positions of the peaks are dependent on temperature. Never-

Fig. 1. Experimental absorption spectra of PPV measured at 80 K (solid curve) and 300 K (dashed curve).

Fig. 2. Experimental PL of PPV measured at 77 K (solid curve) and 300 K (dashed curve).

Fig. 3. Experimental PLE spectra of PPV measured at 77 K (solid curve) and 300 K (dashed curve).

theless, at a fixed temperature, the PLE spectra with fluorescence monitored at the three different peaks as well as at other off-peak regions show no difference in spectral shape and position. Only the absolute intensity is different due to the different intensities of the PL peaks. On the other hand, the absorption or PLE band edge is at around 500 nm. Hence, when the excitation wavelength is close to the luminescence wavelength, the spectrophotometer cannot reject the scattered excitation light. This will cause an upward turning at the low energy side of the PLE spectrum. If the monitored luminescence is at the highest energy peak, which is only 10 to 20 nm away from the absorption band edge, the upward turning feature will smear the spectral structure at the band edge. Therefore, since the spectral characteristics of the luminescence are uniform throughout the luminescence region, it was chosen that the middle PL peak (at about 560–570 nm, depending on the temperature) is monitored. The PLE spectra measured at 77 and 300 K (no temperature controller was used, so there are only data at two temperatures) are shown in Fig. 3.

4. Results and discussion

From Fig. 1, one can see that temperature induces prominent changes in the absorption spectra, which have also been observed previously by other groups. The low-temperature absorption spectrum (80 K) shows much clearer vibronic features and shifts to lower energy when compared with the high-temperature spectrum (300 K). The PL spectra shown in Fig. 2 also exhibit dramatic changes going from 77 to 300 K and the difference is consistent with the absorption spectra, a clear vibronic feature and red band shift at lower temperature. The PLE spectra in Fig. 3 have the same trend as those of absorption spectra. As is already known for PPV polymers, temperature induces PL band shifts and the energy shifted (toward red) is more than 400 cm^{-1} (about 50 meV) in going from room temperature to 10 K [1]. If the blue shift at high temperature is caused by the states populated by the thermal energy at, for example, 300 K, this energy is only about 208 cm^{-1} , which cannot account for the 400 cm^{-1}

shift. Extensive discussions about such phenomena have been given previously [1,8] and two factors were identified which have influence on the spectra: one is the distribution of and the other is the dependence of Huang–Rhys factors, S , on the most important property of PPV, i.e. the conjugation length. In the following theoretical analysis and fitting, we will present a way to incorporate these factors. Our goal is to establish a single theoretical model which could explain experimental absorption, PL and PLE spectra altogether. At the current stage, we attempt this with a qualitative understanding of these experimental spectra.

The concept of conjugation length has played an important role in the study of conducting polymers. It has come about because through it one can relate the properties of polymers to the properties of molecules (oligomers). Oligomers have finite lengths whereas polymers do not; therefore, in choosing the temperature-dependent distribution function of conjugation length, one can come up with discrete or continuous functions. Since the microscopic detail of PPV polymers is not known and we model the systems with oligomers, a simple (discrete) Gaussian distribution of PPV oligomers with different lengths is assumed to be the function, i.e.

$$[N] \propto g(N) = \left(\frac{1}{\pi D}\right)^{1/2} \exp\left[-\frac{(N-N_0)^2}{D}\right] \quad (9)$$

where $[N]$ is the concentration of PPV oligomers with length N (e.g. $N=5$ for pentamers) and D controls the width of distribution. N_0 is the length of oligomers which has maximum concentration at a particular temperature and is dependent on temperature. Considering that the average effective conjugation length of PPV is about 7, N_0 is set to 5 for 300 K and 6 for 77 K, empirically. D is set to 2.5. Note that the values of N_0 and D are chosen in order to produce qualitative agreement with the experimental results and care should be taken that their significance is only at the relative values at different temperatures. The value of $D=2.5$ only demonstrates that contributions from the other oligomers cannot be ignored. The assumption that N_0 decreases with increasing temperature is reasonable since low frequency (less than 208 cm^{-1}) out-of-plane torsional vibrational modes were obtained from our *ab initio* calculations on a trimer model; these modes can be populated at room temperature and cause torsional distortion. The experimental study employing the technique of inelastic incoherent neutron scattering [36] has observed four low-frequency vibrational modes of PPV at 2.5 meV (20 cm^{-1}), 7 meV (56 cm^{-1}), 15 meV (121 cm^{-1}) and 25 meV (202 cm^{-1}). Therefore, the effective conjugation length may decrease when temperature increases due to the thermally induced torsional motion. Temperature effect was also observed for poly(3-hexylthiophene) and its change has been explained by the dependence of chain length on temperature [37,38].

The exact relation between the Huang–Rhys factor and conjugation length is difficult to establish. This is because the Huang–Rhys factor is defined through the square of overlaps

of nuclear wavefunctions. Ideally, one should calculate the equilibrium geometries of ground and excited states of the system, whereby the nuclear overlaps can be evaluated. This task can be achieved with current computing resources only for very small molecules and is not feasible for systems such as PPV. However, from the temperature-dependent experimental absorption and PL spectra, one can propose a simple relation between them as a first approximation. Discussions about the Huang–Rhys factor relating to the degree of conjugation of PPV, based on experimental studies, have been given [1,7,8,39]. It was noted that the Huang–Rhys factor correlates with disorder, that is, the more disorder of the system the larger the Huang–Rhys factor. The dependence of the Huang–Rhys factor on chain length was also demonstrated theoretically by Shuai et al. [40]. Since disorder decreases the conjugation length of PPV and increases the Huang–Rhys factor, the following relation is chosen:

$$S = a \exp\left(-\frac{N^2}{b}\right) \quad (10)$$

where a and b are empirically chosen to be 3.2 and 38, respectively. Note that when the conjugation length, N , approaches infinity, S becomes zero. The a and b are chosen so as to produce reasonable S values judging from the experimental PL and PLE spectra, i.e. for $N=5$, $S=1.66$, for $N=6$, $S=1.24$, and for $N=8$, $S=0.59$.

The values of $|\mu_{ba}|^2$ and $\bar{\omega}_{ba}$ have been calculated using molecular orbital theories [25] and are listed in Table 1. A plot of $\bar{\omega}_{ba}$ versus N is shown in Fig. 4 and a fitted equation is obtained:

$$\hbar\bar{\omega}_{ba} = \frac{2.14}{N} + 2.84 \text{ eV} \quad (11)$$

This equation is used to calculate $\bar{\omega}_{ba}$ for $N \geq 7$ and similar (linear) extrapolation is done for $|\mu_{ba}|^2$. The total absorption is calculated by summing contributions from oligomers of different lengths:

$$\alpha_T(\omega) = \sum_{i=N_{\min}}^{N_{\max}} \alpha_i(\omega) [i] \quad (12)$$

where $N_{\min}=3$, $N_{\max}=8$. The theoretically calculated absorption spectra of PPV at 80 K and 300 K are shown in Fig. 5. One can notice that the change in spectra due to temperature in Fig. 5 qualitatively agrees with that shown in Fig. 1. The reason for this change, from the theoretical analysis, is mainly due to the shift in the Gaussian distribution (Eq. (9)) since, when the temperature is lowered, the conjugation length becomes longer due to weaker conformational disorder. The 5000 cm^{-1} energy shift applied to the semi-empirically obtained $\bar{\omega}_{ba}$ is used to account for the error that is introduced through modeling polymers by gas phase oligomer calculations, such as the solvation stabilization and interchain interaction. This discrepancy between experimental and theoretical spectra is one of the difficulties need to be resolved before one can achieve quantitative analysis. The width of

Table 1

Excitation energies and transition moments of ground to first excited states of PPV oligomers

Oligomer (N)	$\bar{\omega}_{ba}$ (eV)	$ \mu_{ba} ^2$ (debye ²)
1	4.99	30.3
2	3.88	93.5
3	3.53	158.9
4	3.36	221.3
5	3.27	282.9
6	3.21	344.0

Fig. 4. Dependence of ground to excited state transition energies on PPV oligomer length calculated from MO theory.

Fig. 5. Calculated absorption spectra at 80 K (solid curve) and 300 K (dashed curve). The energies are shifted 5000 cm^{-1} lower than that obtained from Eq. (11). $\omega_p = 1681 \text{ cm}^{-1}$, d (in Eq. (7)) = 650 cm^{-1} .

inhomogeneity $d = 650 \text{ cm}^{-1}$ for 300 K is consistent with the width obtained for unoriented PPV film at room temperature [41]. Research of conformational effects on inhomogeneity has been performed and values of d for different types of PPV films were measured [8]. It was observed that high-temperature spectra have wider width than those of low-temperature ones and PL spectra have narrower width than absorption spectra. The reason for such inhomogeneity has been analyzed in terms of random walks of neutral excitations

through inhomogeneously broadened density of states in three dimensions.

Recently, an experimental and theoretical investigation of PPV oligomers has been carried out by Cornil et al. [32], in which two effective vibrational modes were employed in the theoretical analysis of oligomer absorption spectra. The requirement of two effective vibrational modes can be seen clearly from the slightly resolved shoulder in the $S_1 \rightarrow S_0/0 \rightarrow 1$ vibronic band in the low-temperature experimental PL spectra. Since the focus of this study is on the temperature effect, we restricted ourselves to using one effective vibrational mode, at 1681 cm^{-1} , which is chosen according to the ab initio calculations [31]. Note that the $S = 1.66$ for pentamer in this study is consistent with the $S_{\text{tot}} = 1.60$ for PPV5 in Ref. [32].

Next we will focus on the calculation of PLE spectra. A simple kinetic model was given recently to explain the smaller intensity and narrower bandwidth compared to absorption spectra [31]. In this study a more detailed kinetic model is given as the following (using pentamer as an example).

Step 1 is absorption of one photon by a pentamer, which becomes an excited species. Step 2 represents the exciton migration to a site with lower energy (here a hexamer). Step 3 is vibrational relaxation of the excited pentamer. Step 4 is PL. Step 5 is the non-radiative decay process. Step 6 is the formation of interchain excimer. Step 7 is the formation of interchain exciplexes (polaron pair). The rate equations according to the above model are

$$\begin{aligned} \frac{d[M_5^*]}{dt} &= k_a^5[M_5] - k_{\text{hop}}^5[M_5^*] - k_v^5[M_5^*] \\ &\quad - k_{\text{nr}}^5[M_5^*] - k_{\text{em}}^5[M_5^*] + k_{\text{hop}}^4[M_4^*] \\ \frac{d[M_5^\pm]}{dt} &= k_v^5[M_5^*] - k_{\text{em}}^5[M_5^\pm] \\ \frac{d[(M-M)_5^*]}{dt} &= k_{\text{et}}^5[M_5^*] - k_v^5[(M-M)_5^*] \end{aligned} \quad (13)$$

Note that there is an extra term, $k_{\text{hop}}^4[M_4^*]$, in Eqs. (13) since there is also a similar set of processes for tetramers, and a tetramer exciton can migrate to a pentamer exciton.

Applying a steady-state approximation, one can obtain the PLE intensity due to pentamers as

$$\begin{aligned} I_{\text{PLE}} &= k_{\text{em}}^5[M_5^\pm] = k_v^5[M_5^*] \\ &= \frac{k_v^5 k_a^5}{k_{\text{hop}}^5 + k_v^5 + k_{\text{et}}^5 + k_{\text{nr}}^5} [M_5] + \frac{k_v^5 k_{\text{hop}}^4}{k_{\text{hop}}^5 + k_v^5 + k_{\text{et}}^5 + k_{\text{nr}}^5} [M_4^*] \end{aligned} \quad (14)$$

Note that Eq. (14) still depends on the concentration of excited tetramers and it has to be calculated. The generalized concentration of excited oligomers from the kinetic model is

$$\begin{aligned} [M_n^*] &= \frac{k_a^n}{k_{\text{hop}}^n + k_v^n + k_{\text{et}}^n + k_{\text{nr}}^n} [M_n] \\ &\quad + \frac{k_{\text{hop}}^{n-1}}{k_{\text{hop}}^n + k_v^n + k_{\text{et}}^n + k_{\text{nr}}^n} [M_{n-1}^*] \end{aligned} \quad (15)$$

and the total PLE intensity emitting from the $N=n$ PPV segment is

$$\begin{aligned} I_{\text{PLE}} &= k_{\text{em}}^n [M_n^\pm] = \frac{k_v^n}{k_{\text{hop}}^n + k_v^n + k_{\text{et}}^n + k_{\text{nr}}^n} \left\{ k_a^n [M_n] \right. \\ &\quad \left. + \sum_{i=1}^{n-1} \left\{ \prod_{j=1}^i \frac{k_{\text{hop}}^{n-j}}{k_{\text{hop}}^{n-j} + k_v^{n-j} + k_{\text{et}}^{n-j} + k_{\text{nr}}^{n-j}} \right\} k_a^{n-i} [M_{n-i}^*] \right\} \end{aligned} \quad (16)$$

At a first glance of the above equation, the calculation of PLE spectra is not feasible since k_{hop} , k_v , k_{nr} and k_{et} are not known. However, one can calculate qualitative PLE spectra. The vibrational relaxation rate in PPV was estimated to be less than 200 fs [15,16] and the total rate of photon energy relaxation processes can be as fast as 250 fs [16]. Since the detailed mechanisms of electron transfer, exciton migration and non-radiative decay processes are not known and they all relate to the redistribution of electron densities, it is assumed that $k_{\text{et}}^n = k_{\text{hop}}^n = k_{\text{nr}}^n$. From the experimental observation that $k_v^n > (k_{\text{et}}^n + k_{\text{hop}}^n + k_{\text{nr}}^n)$, we tentatively assign $k_v^n = 4k_{\text{et}}^n$. Hence, when PPV is excited to trimer energy levels, the PLE intensity is

$$\begin{aligned} I_{\text{PLE}} &= \frac{4}{7} k_a^8 [M_8] + \frac{4}{7} \frac{1}{7} k_a^7 [M_7] + \frac{4}{7} \left(\frac{1}{7} \right)^2 k_a^6 [M_6] \\ &\quad + \cdots + \frac{4}{7} \left(\frac{1}{7} \right)^5 k_a^3 [M_3] \end{aligned} \quad (17)$$

From the above equation, one can see that the major contribution to the PLE intensity comes from emission from longer PPV segments. Substituting Eq. (9) and $k_a = \alpha_n(\omega)$ into Eq. (17), the theoretical PLE spectra at 77 and 300 K are shown in Figs. 6 and 7, respectively. Comparing between Figs. 6(a) and 7(a), it is clear that temperature has a smaller influence on the PLE spectra than on the absorption spectra and that low-temperature PLE has a somewhat narrower bandwidth than that of the high-temperature one. These trends are consistent with the experimental results shown in Fig. 3.

Fig. 6. Calculated PLE spectra at 77 K: (a) PLE; (b) PLE (dashed curve) compared with absorption (solid curve).

For the theoretical calculation of PL, if all the excited states emit photons simultaneously, the total emission intensity would be a sum of all emission coming from these states:

$$I_T(\omega) = \sum_{i=N_{\min}}^{N_{\max}} I_i(\omega) [i] \quad (18)$$

However, when one recognizes the fact that, for PPV, the emission comes mainly from lower excited states (longer PPV chain) after exciton migration [8,41], it is only necessary to calculate the emission coefficient for the lower states. Since we have assumed a Gaussian distribution of PPV chain lengths, it is not sufficient to consider emission coming solely from the lowest excited state. Due to the lack of information about the balance between material morphology and kinetic dynamics, a reasonable estimate of Eq. (18) can be taken by summing the PL coming from the long PPV segments. The weighting factors for these segments can be approximated by considering the Gaussian distribution factors. For example, at 77 K, hexamers have the highest distribution and, when they are excited, a fraction of 0.20 excitons can quickly migrate to octamers since there are only 20% octamers compared to hexamers, a fraction of 0.67 can migrate to heptamers, leaving only a fraction of 0.13 of excited hexamers. Together these segments emit light and the total emission intensity is

Fig. 7. Calculated PLE spectra at 300 K.

$$I_T(\omega) = \text{constant}$$

$$\times [0.20I_8(\omega) + 0.67I_7(\omega) + 0.13I_6(\omega)] \quad (19)$$

For excitation to other high energy PPV segments, the excitons all migrate to octamers and heptamers to emit light and the emission shape will be buried underneath that of Eq. (19). At 300 K, similar approximations lead to the following equation:

$$I_T(\omega) = \text{constant} \times [0.03I_8(\omega) + 0.20I_7(\omega) + 0.67I_6(\omega) + 0.10I_5(\omega)] \quad (20)$$

Fig. 8. Calculated PL at 77 K (solid curve) and 300 K (dashed curve). d (in Eq. (8)) = 390 cm^{-1} for 77 K and 530 cm^{-1} for 300 K.

The calculated PL spectra according to Eqs. (19) and (20) are shown in Fig. 8. One can see the qualitative agreement of the emission features with the experimental spectra shown in Fig. 2. The vibronic intensity shifts to $0 \rightarrow 1$ at 300 K due to more emission from pentamers which have larger S . In the theoretical spectra, the intensity drop for the $0 \rightarrow 3$ transition compared to the $0 \rightarrow 2$ transition is not as great as that observed experimentally. This is expected since only one effective vibrational mode is used. If two effective vibrational modes were used in the analysis, as has been done previously [32], the total Huang–Rhys factor is distributed between them and the vibronic bands with higher vibrational quanta will have larger intensity drop than smaller vibrational quanta bands, which would make the theoretical spectra agree better with the experiments.

5. Conclusions

Temperature causes change in the spectral features of PPV in a way which could not be explained solely by a molecular theory which considers only the Boltzmann average of a system. Such an extent of temperature effect could be due to the polymeric nature of PPV. As demonstrated in this study, the simplest way to model such a system, although speculative, is to impose two assumptions: a Gaussian distribution of PPV chain lengths and the dependence of Huang–Rhys factors on the chain length. With these empirical assumptions and the theoretical models for molecular systems, satisfactory agreement between theoretical and experimental results can be obtained.

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