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The absorption and emission spectra of 1,4-di(2-phenylvinyl)benzene. A theoretical analysis

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Abstract. The ground and excited states of 1,4-di(2-phenylvinyl)benzene (PPV3) were studied theoretically and compared with experimental results. The equilibrium geometries of the ground states were found to be nonplanar despite the π conjugation in PPV3; however, the equilibrium geometry of the first excited state of PPV3 is planar, due to the increased π character between the benzene and ethylene units. The electronic structures of the excited state were investigated using the INDO/S-CIS method. The lack of a mirror-image relationship between the absorption and fluorescence spectra of PPV3, obtained experimentally, was analyzed theoretically. It was demonstrated that structural inhomogeneity might be the reason for the particular spectral band shape.

Key words: Spectroscopy – poly(*p*-phenylene vinylene) – ZINDO

1 Introduction

Recently, organic light-emitting materials have attracted much attention. Among these materials, poly(*p*-phenylene vinylene) (PPV) has been studied extensively due to its wide range of processibility and electroluminescence [1, 2]. Both experimental [1–5] and theoretical [5–12] research has been performed in order to understand the properties of PPV. Theoretical studies using different theories have satisfactorily explained the geometrical and electronic structures. The potential barrier of torsional motion along the carbon–carbon backbone was calculated to be small [5, 11]. The effect of different functional groups on the band-gap energy between the conduction and valence bands has been characterized [12]. The dependence of the energy of the excited states on the conjugation length has been studied using molecular orbital (MO) theory [6, 7, 9] and the temperature effect on the spectral shape of the absorption and emission spectra has been simulated based on properties of PPV oligomers [8]. These studies have informed us that the geometrical structure of PPV polymer is complicated and the simple theoretical model that one can resort to is to take into account the different conjugation lengths in the polymer. Hence, one would gain better understanding of the material if properties of PPV oligomers were analyzed in detail.

By synthesizing PPV oligomers of different sizes and studying their optophysical properties in solutions, one might expect to obtain clearer information since, firstly, the effect of conjugation length has been removed and, secondly, the interchain interaction is absent in dilute solutions. Based on these reasons, the absorption and fluorescence spectra of, for example, 1,4-di(2-phenylvinyl)benzene (PPV3), shown in Fig. 1, should demonstrate a better mirror image of each other than those obtained for PPV films. The experimental absorption and fluorescence spectra of PPV3 are shown in Fig. 2. What interests us is that these spectra are far from mirror images of each other. Actually, they resemble the absorption and fluorescence of PPV film.

Such a result is quite surprising since dilute solutions of organic molecules usually show mirrorlike absorption and fluorescence spectra, for example, perylene [13]. In this paper, the possible reason for the non-mirror-image appearance of the spectra is presented. Molecular spectroscopic theory is used to analyze the experimental results. By obtaining good theoretical fitting, we speculate that there are structural isomers of PPV3 present in the sample.

2 Theory and computation

The molecular absorption coefficient for the electronic transition from state a to state b is given by [14]

$$\alpha_{\mathrm{ab}}(\omega) = \frac{4\pi^2\omega}{3ac\hbar}|\vec{\mu}_{\mathrm{ba}}|^2 \times \sum_{v}\sum_{v'} P_{\mathrm{a}v}|\langle\Theta_{\mathrm{b}v'}|\Theta_{\mathrm{a}v}\rangle|^2\delta(\omega_{\mathrm{b}v',\mathrm{a}v} - \omega) \ , \tag{1}$$

where a is a factor which describes the medium effect, v and v' are the vibrational quantum numbers, $\vec{\mu}_{\mathrm{ba}}$ is the

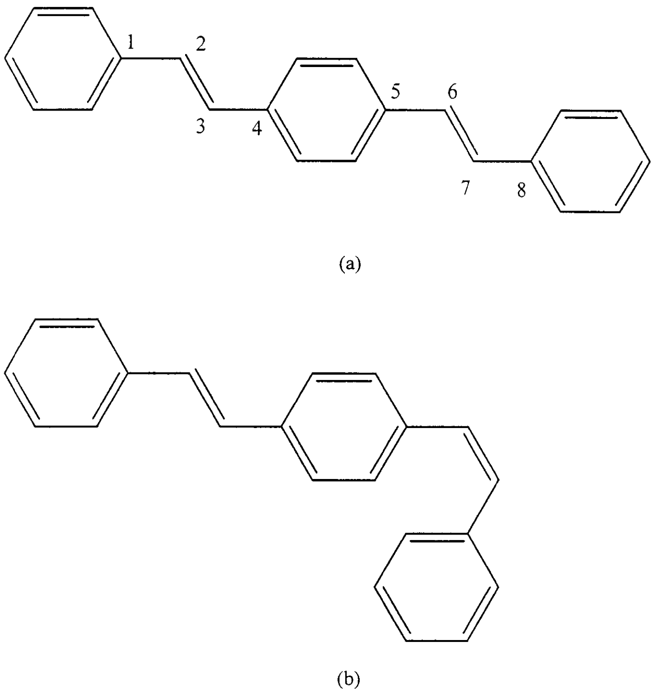


Fig. 1a, b. Isomers of 1,4-di(2-phenylvinyl)benzene (*PPV3*). **a** trans–trans, **b** trans–cis

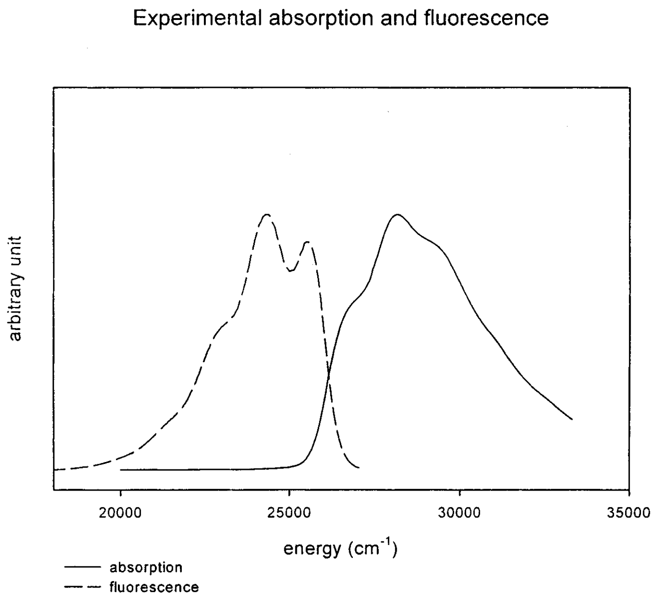


Fig. 2. Experimental absorption (*solid line*) and fluorescence (*dashed line*) spectra of PPV3

electronic transition moment, P_{av} is the Boltzmann distribution function, and $|\langle\Theta_{bv'}|\Theta_{av}\rangle|^2$ is the Franck–Condon factor. The emission intensity for the electronic transition from state b to state a is given by

$$I_{ba}(\omega) = \frac{4a\omega^3}{3\hbar c^3}|\vec{\mu}_{ba}|^2 \times \sum_v \sum_{v'} P_{bv'}|\langle\Theta_{bv'}|\Theta_{av}\rangle|^2\delta(\omega_{bv',av}-\omega) \ . \qquad (2)$$

Using the integral form of the delta function, the absorption coefficient is expressed as

$$\alpha_{ab}(\omega) = \frac{2\pi\omega}{3ac\hbar}|\vec{\mu}_{ba}|^2 \times \int_{-\infty}^{\infty} \mathrm{d}t \sum_v \sum_{v'} P_{av}|\langle\Theta_{bv'}|\Theta_{av}\rangle|^2 \times \exp\left[it(\omega_{bv',av}-\omega)\right] \ , \qquad (3)$$

where the Boltzmann distribution for a single harmonic vibrational mode is

$$P_{av} = \frac{\exp\left\{-\left[E_a + \left(v+\frac{1}{2}\right)\hbar\omega_v\right](kT)^{-1}\right\}}{\sum_v \exp\left\{-\left[E_a + \left(v+\frac{1}{2}\right)\hbar\omega_v\right](kT)^{-1}\right\}} \ , \qquad (4)$$

where E_a is the ground-state energy of the harmonic potential and ω_v is the frequency of the vibrational mode.

Using harmonic oscillator functions for nuclear wavefunctions of the ground and excited states in Eq. (3), the absorption coefficient, for the single-mode case, can be transformed into the following form

$$\alpha_{ab}(\omega) = \frac{2\pi\omega}{3\hbar c}|\vec{\mu}_{ba}|^2 \int_{-\infty}^{\infty} \mathrm{d}t \exp\{it(\omega_{ba}-\omega) - S\left[(\bar{n}+1)\left(\mathrm{e}^{-it\omega_v}-1\right) + \bar{n}\left(e^{it\omega_v}-1\right)\right]\} \ , \qquad (5)$$

where

$$\bar{n} = \frac{1}{\exp\left(\frac{\hbar\omega_v}{kT}\right) - 1} \qquad (6)$$

and S is the Huang–Rhys factor. In order to include the properties in the condensed phase, inhomogeneity due to molecules in different orientations and environments should be included. When a Gaussian distribution of ω_{ba} is considered,

$$g(\omega_{ba}) = \frac{1}{\sqrt{2\pi d^2}}\exp\left[-\frac{(\omega_{ba}-\bar{\omega}_{ba})^2}{2d^2}\right] \ , \qquad (7)$$

Eq. (5) becomes

$$\alpha_{ab}(\omega) = \frac{2\pi\omega}{3\hbar c}|\vec{\mu}_{ba}|^2 \int_{-\infty}^{\infty} \mathrm{d}t \exp\left\{it(\bar{\omega}_{ba}-\omega) - \frac{d^2t^2}{4} + S\left[(\bar{n}+1)\left(\mathrm{e}^{-it\omega_v}-1\right) + \bar{n}\left(\mathrm{e}^{it\omega_v}-1\right)\right]\right\} \ , \qquad (8)$$

where $\bar{\omega}_{ba}$ represents the average electronic transition energy after averaging molecules in different environments. A similar equation can be obtained for $I_{ba}(\omega)$.

The ground-state equilibrium geometries of PPV3 were calculated at the self-consistent-field level using the 6-31G basis sets in GAUSSIAN94 [15]. The equilibrium geometry of the first excited state was also obtained from ab initio calculations. These optimized geometries were confirmed by their all-positive vibrational frequencies. To simplify the problem of modeling structural inhomogeneity in the sample, it was assumed that there are two types of PPV3 present, trans–trans and trans–cis forms, as shown in Fig. 1.

Using the optimized structures, the electronic structures of the excited states were calculated using configuration interaction (CI) theory using the INDO/S Hamiltonian [16, 17]. A total of 225 monoexcited Slater determinants were generated from 15 occupied MO and 15 unoccupied MO, of which 121 are π MO excitations. The adequacy of this CI space was discussed previously [6].

In the calculation of the band shapes of the spectra, numerical values of the frequency of the vibrational mode, the coupling constant, and the inhomogeneity were first determined for the experimental fluorescence, where emission is attributed to trans–trans PPV3. By fixing these values for trans–trans PPV3, the necessary para- meters for trans–cis PPV3 were determined according to the experimental absorption spectra.

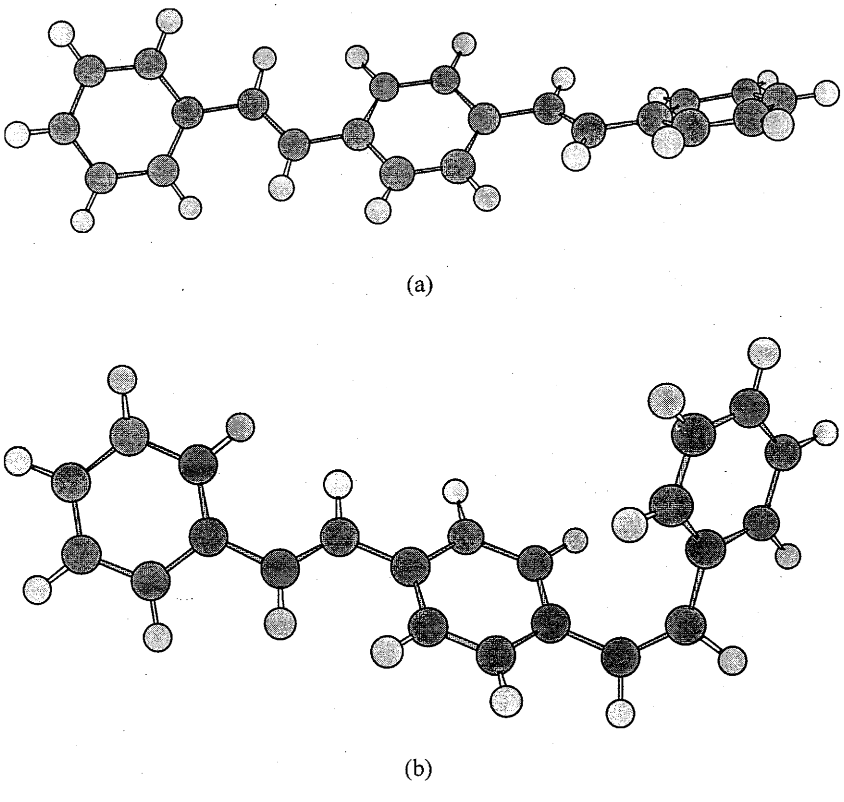
3 Results and discussion

The fully optimized structures of trans–trans and trans–cis PPV3 are shown in Fig. 3 and some structural data are given in Table 1. As seen clearly from the figure, both of them are not planar. The nonplanar structure of trans–trans PPV3 departs from the usual expectation of planar geometry for π-conjugated organic molecules. These results could be expected since among the 11 occupied π MO and 11 unoccupied π MO, only one MO has no nodal plane and twisting out of plane gradually will not influence the total energy much, while lowering the steric repulsion between neighboring hydrogens at the same time. The trans–trans form is more stable than the trans–cis form by 1506 cm^{-1} according to the ab initio calculations. The geometry of the first excited state is shown in Fig. 4 with some structural data given in Table 1. Note that the structure is planar. This is because the major monoexcited configuration contributing to the first excited state is the highest occupied MO (HOMO) to Lowest unoccupied MO (LUMO) excitation, shown in Fig. 5. The HOMO has π antibonding character between C_1C_2, C_3C_4, C_5C_6, C_7C_8, whereas the LUMO has π bonding character between C_1C_2, C_3C_4, C_5C_6, C_7C_8. Hence the net result of the HOMO-to-LUMO excitation is the increased π bonding between C_1C_2, C_3C_4, C_5C_6, C_7C_8, and planar geometry is favored. The shortening of bonds C_1C_2, C_3C_4, C_5C_6, C_7C_8 accompanied by the lengthening of C_2C_3 and C_6C_7 can been seen by comparing data in Table 1.

The oscillator strengths versus excitation energy of trans–trans and trans–cis PPV3 obtained from INDO/S-CI calculations are shown in Fig. 6. The numerical values are given in Table 2. The calculated first excited state of trans–trans PPV3 lies at a lower energy than that of the trans–cis form: the energy difference is 1196 cm^{-1}. A combined plot of the experimental absorption spec-

Table 1. Bond lengths of optimized 1,4-di(2-phenylvinyl)benzene (*PPV3*). Refer to Fig. 1 for the numbering of the atoms

Bond length (Å)	C_1C_2	C_2C_3	C_3C_4	C_5C_6	C_6C_7	C_7C_8
Trans–trans	1.474	1.332	1.472	1.472	1.332	1.474
Trans–cis	1.474	1.332	1.473	1.480	1.333	1.482
First excited state (trans–trans)	1.438	1.374	1.416	1.416	1.374	1.438


(a)

(b)

Fig. 3a, b. Equilibrium geometries of PPV3. **a** trans–trans, **b** trans–cis

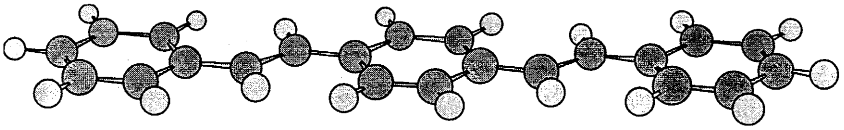
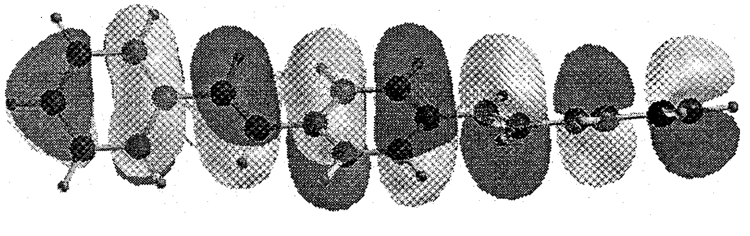
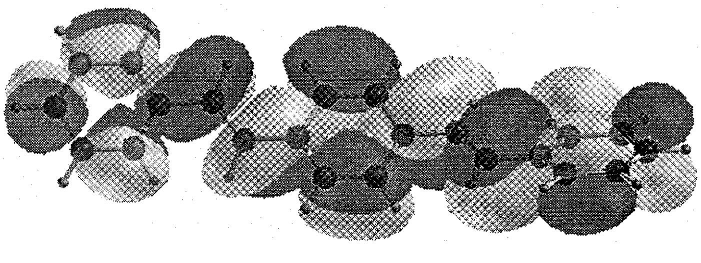


Fig. 4. Optimized geometry of the first excited state of PPV3



HOMO



LUMO

Fig. 5. Plots of the highest occupied molecular orbitals (*HOMO*) and the lowest unoccupied molecular orbitals (*LUMO*) of PPV3 from ab initio calculations

Table 2. Excitation energies and oscillator strengths of PPV3

Excited state	Trans–trans PPV3		Trans–cis PPV3	
	Excitation energy (cm^{-1})	Oscillator strength	Excitation energy (cm^{-1})	Oscillator strength
1	31483	2.011	32679	1.456
2	34125	0.019	34412	0.011
3	35901	0.002	35918	0.006
4	35914	0.005	36349	0.001
5	38294	0.014	38671	0.248
6	42329	0.000	42594	0.015
7	43781	0.095	43778	0.058
8	46379	0.311	46364	0.266
9	46962	0.052	46632	0.311
10	47527	0.200	47630	0.024
11	47653	0.341	47688	0.245
12	48309	0.081	47989	0.079
13	50340	0.498	49349	0.142

trum scanned up to about 42 000 cm^{-1} and data in Fig. 6 is shown in Fig. 7. In this plot, theoretical excitation energies were all shifted by 5000 cm^{-1} to lower energy, to account for the medium effect as was done previously [7]. The results from theoretical calculations agree with experimental data fairly well.

By looking at Fig. 7, one can come to a tentative conclusion that electronic excitations of both trans–trans and trans–cis PPV3 contribute to the absorption spectra. Hence, in the following spectral analysis, fluorescence is attributed to coming from trans–trans PPV3 and absorption is the sum of the absorption of the trans–trans and trans–cis forms. It is assumed that trans–cis PPV3 does not emit light and that when it is excited the energy is transferred to trans–trans PPV3. The vibronic coupling frequency, ω_v, coupling constants, S, and inhomogeneity, d, were adjusted according to the experimental fluorescence. The theoretical and experimental fluorescence spectra of PPV3 are shown in Fig. 8. The parameters used are $\omega_v = 1350\,\mathrm{cm}^{-1}$, $S = 1.32$, and $d = 760\,\mathrm{cm}^{-1}$. The agreement between theory and experiment is quite good, strongly suggesting that experimental emission is only due to trans–trans isomers.

The theoretical absorption was obtained using the equation

$$\alpha(\omega) = \alpha_{\mathrm{TT}}(\omega) + m \times \alpha_{\mathrm{TC}}(\omega) \ , \qquad (9)$$

where m is a parameter which controls the relative contributions of $\alpha_{\mathrm{TT}}(\omega)$ and $\alpha_{\mathrm{TC}}(\omega)$. $\alpha_{\mathrm{TT}}(\omega)$ and $\alpha_{\mathrm{TC}}(\omega)$ designate the absorption coefficients of trans–trans and trans–cis PPV3, respectively. Note that the values of $\bar{\omega}_{\mathrm{ba}}$ in Eq. (8) are different for $\alpha_{\mathrm{TT}}(\omega)$ and $\alpha_{\mathrm{TC}}(\omega)$. Based on the INDO/S-CI calculations and the energy shift applied for the medium effect, $\bar{\omega}_{\mathrm{ba}}^{\mathrm{TT}} = 26483\,\mathrm{cm}^{-1}$ and $\bar{\omega}_{\mathrm{ba}}^{\mathrm{TC}} = 27679\,\mathrm{cm}^{-1}$. Using $S = 1.32$ for trans–trans PPV3 and assuming the same vibrational frequency of 1350 cm^{-1} for both isomers, S for trans–cis PPV3, m in Eq. (9), and the inhomogeneity were determined according to the experimental absorption. The theoretical and experimental absorption spectra are shown in Fig. 9. The coupling constant for trans–cis PPV3 was determined to be 1.60, which is higher than the value of the trans–trans form. This results is consistent with the concept stating that the higher the disorder, the stronger the coupling constant [3, 8]. The inhomogeneity was 900 cm^{-1}. The nature of the structural inhomogeneity,

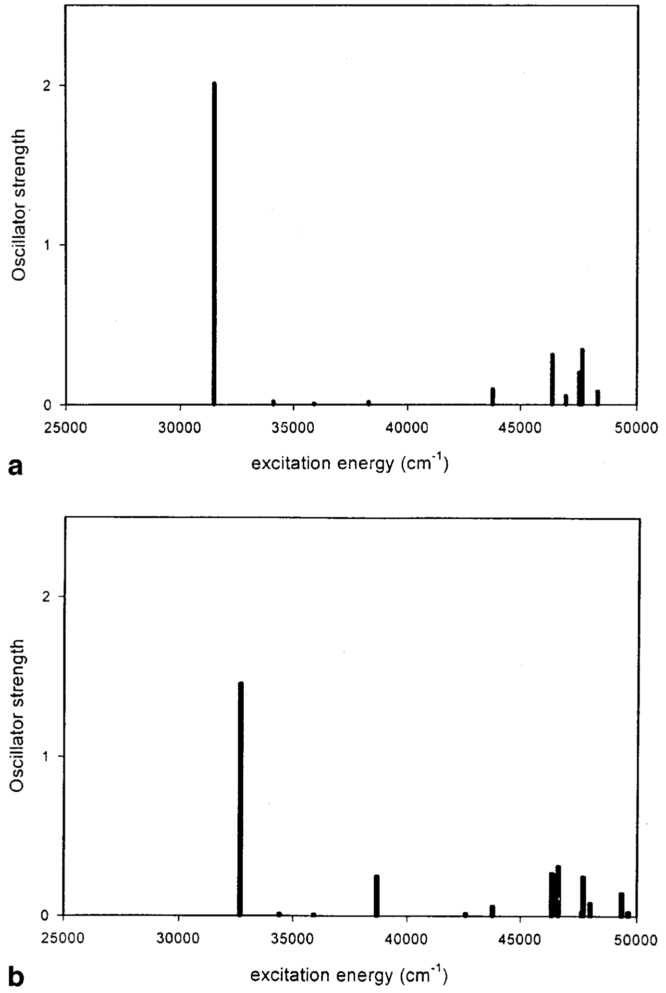


Fig. 6. Oscillator strengths versus excitation energies of **a** trans–trans and **b** trans–cis PPV3

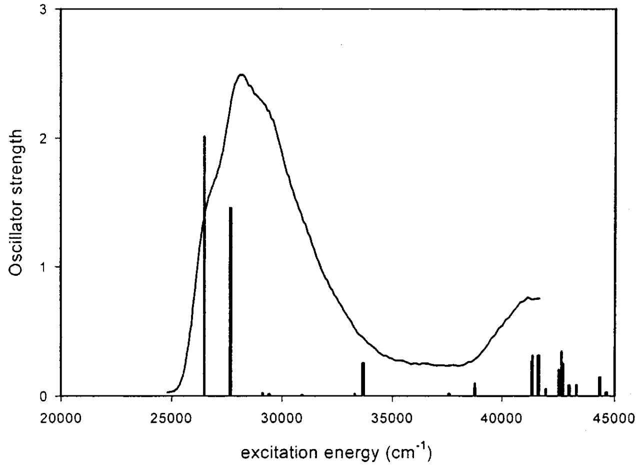


Fig. 7. A combined plot of experimental absorption and (trans–trans + trans–cis) PPV3 oscillator strengths

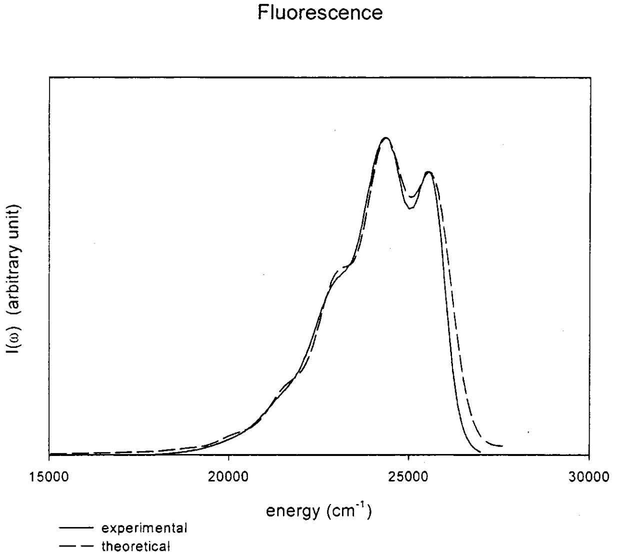


Fig. 8. Experimental (*solid line*) and theoretical (*dashed line*) fluorescence spectra of PPV3

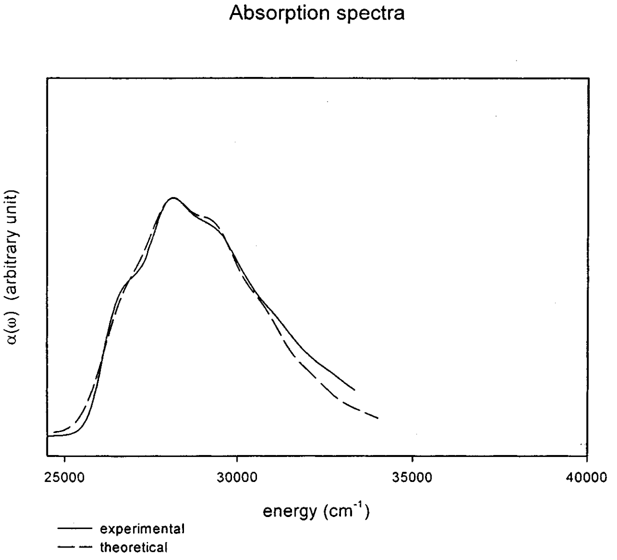


Fig. 9. Experimental (*solid line*) and theoretical (*dashed line*) absorption spectra of PPV3

such as the amount of PPV with different effective conjugation lengths and different structural isomeric units, has not been studied experimentally in detail. Therefore, from the theoretical analysis given here, one can provide some insight into the distribution of structural isomers in this oligomer sample. Based on the ratio of the square of transition moments, $\vec{\mu}_{ba}^{2}$, of trans–trans and trans–cis PPV3, calculated from the INDO/S-CI calculations, and the percentage contribution of these isomers to the absorption spectrum, it can be deduced that the mole fraction of trans–trans PPV3 in the sample is about 0.64; however, one should note that the theoretical analysis provided in this study does not prove exclusively that the mole fraction of trans–trans PPV3 in the sample is indeed 0.64. There are other theoretical methods for treating the experimental spectral shape. For example, the cis–cis form of PPV3 is not considered here and it may also be present in the sample, although maybe in very minute amounts. Another theoretical treatment, employing displaced and distorted potentials, could also provide an explanation for the non-mirror-like absorption and emission. This theory has been applied to 1,4-bis[2-(3,4,5-trimethoxyphenyl) ethenyl]benzene oligomers recently with satisfactory results [18]. It is our hope that these theoretical studies will trigger more experimental work on the structure of PPV at the molecular level, and that more advanced processing technology will be developed.

4 Conclusions

The optimized ground and first excited states of PPV3 were obtained from ab initio calculations. The energy positions and oscillator strengths of the excited states calculated from semiempirical theory agree well with the experimental data. By assuming that energy transfer from trans–cis to trans–trans PPV3 occurs, the absorption and emission spectra can be constructed theoretically. Parameters such as coupling constants and inhomogeneities were determined accordingly. The agreement between theory and experiment strongly suggests that this simple model elucidates the nature of this material.

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