

Site-Selective Fluorescence Spectroscopy of Conjugated Polymers and Oligomers

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Received February 12, 1998

1. Introduction

Inhomogeneous broadening is a ubiquitous property of absorption and fluorescence spectra of chromophores, both organic and inorganic, embedded in random matrices. It originates from random local variations of that contribution to the transition energy that is governed by the interaction of the excited state with its polarizable environment. The elimination of that broadening has been a central endeavor of research into spectroscopic problems of random solids like glasses or polymers. It requires the selection of a certain subensemble of chromophores or, in the extreme case, of single molecules via appropriate methods like spatially or spectrally confined excitation and its photophysical characterization. One of these methods involves hole burning.¹ It is premised on the condition that a chromophore undergoes a photochemical or photophysical reaction after excitation that removes it from its original spectroscopic site. Site-selective fluorescence spectroscopy (SSFS) is an alternative method applicable to fluorescent chromophores. It is the purpose of this Account to give an overview of the underlying principle and to discuss recent advances concerning excited state phenomena in conjugated polymers and oligomers.

2. Theoretical and Experimental Background

Upon electronic excitation the charge distribution of a molecule will change as do the molecular forces. As a response to that change the molecular skeleton will vibrate and relax into a new equilibrium configuration. There will

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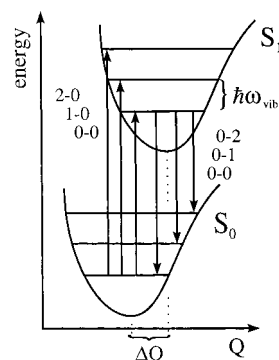


FIGURE 1. Illustration of the Franck Condon principle for absorption $S_1 \leftarrow S_0$ 0–0 and emission $S_1 \rightarrow S_0$ 0– n . The configurational displacement ΔQ between S_0 and S_1 determines the intensity of the particular transitions.

be a concomitant change of the intermolecular configuration as well. As far as vibronic processes are concerned the situation can be illustrated in terms of the Franck Condon principle (Figure 1). Optical transitions occur between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Recall that if there were no readjustment of the bond lengths, i.e., no displacement of the potential energy curve in the excited state relative to the ground state, only a single absorption line—corresponding to the $S_1 \leftarrow S_0$ 0–0 transition—would be allowed for reasons of orthogonality of the vibrational wave functions. In the case of coupling to a single harmonic oscillator of reduced mass M and angular frequency ω the strength of coupling is described by the Huang–Rhys factor

$$S = \frac{M\omega}{2\hbar}(\Delta Q)^2 \quad (1)$$

ΔQ being the displacement of the minima of the potential curve along the configurational coordinate upon electronic excitation. In this case the absorption spectrum consists of an electronic origin, the $S_1 \leftarrow S_0$ 0–0 line, followed by a vibronic replica, $S_1 \leftarrow S_0$ $n \leftarrow 0$, whose normalized intensity distribution, I_n , is a Poissonian mapping the overlap between the vibrational wave functions,

$$I_n = S^n e^{-S} / n! \quad (2)$$

For $S > 1$ it has a maximum at an energy $S\hbar\omega$ above the electronic origin band. For large values of S , I_n approaches a Gaussian with variance $\hbar\omega S^{1/2}$. Thus, S is a crude measure of the number of vibrations generated when the excited molecule relaxes from its ground state configuration to the new equilibrium configuration in the excited state and $S\hbar\omega$ is the relaxation energy. The value of S can be inferred either from the fractional intensity of the 0–0 transition

$$I_{0-0} / \sum_{n=0}^{\infty} I_{n-0} = e^{-S} \quad (3)$$

or from

$$I_{1-0}/I_{0-0} = S \quad (4)$$

In general, ω is different in the ground and excited states and potentials are not exactly parabolic. For large molecules the concomitant modifications in the above scheme are small, though. Of greater importance is the fact that there are several vibrational modes that couple to an electronic transition. Equations 1 and 2 can be applied to each individual vibrational mode i associated with the Huang–Rhys factor S_i , the total Huang–Rhys factor being $S = \sum_i S_i$. If a particular vibronic line carries the same intensity as the 0–0 line, the S_i value of that mode would be 1. It is important to note that observing the 0–0 line in an absorption/emission spectrum is all but a signature of no configurational relaxation occurring. The total relaxation energy is

$$E^{\text{rel}} = \sum S_i \hbar \omega_i \quad (5)$$

Fluorescence as well as absorption spectra—recorded in the form of fluorescence excitation spectra—of gas phase molecules are in accord with the above notion. A beautiful example is the work of Amirav et al. on a jet-cooled molecular beam of tetracene.² It reveals the rich vibrational spectrum of a large π -conjugated molecule. Spectra of aromatic molecules recorded in a fluid or solid noncrystalline matrix are much broader, and most of the vibronic structure is lost. Often only a single vibronic feature and its overtones, representing, in fact, the convolution of the contribution of several strong modes such as phenyl ring vibrations, can be distinguished. One reason for this loss of structure is the interaction of the excited state dipole with the solvent molecules. Due to the change in dipole moment after electronic excitation the solvent cage surrounding a chromophore reorganizes. The statistical nature of this effect leads to line broadening while the relaxation of the solvent cage into its new equilibrium configuration gives rise to a Stokes shift between absorption and emission. In frozen solution in which solvent molecules are randomly distributed yet spatially fixed, inhomogeneous spectral broadening reflects the locally varying van der Waals interaction energy (i.e., the solvent shift) of an excited chromophore with its neighbors.³ Another contribution may result from some configurational disorder of the chromophore itself. Prominent examples are conjugated polymers in which conjugation is interrupted by kinks, twists, or accidental local chemical modification.⁴ The statistically varying length of the segment translates into a distribution of transition energies via basically a particle in a box argument. Both types of disorder can be superimposed and give rise to an inhomogeneously broadened distribution of site energies, in the ground as well as in the excited state(s). Absorption and emission spectra map the convolution of both distributions. If their width becomes comparable to the vibrational spacing, vibronic structure of the spectra will be lost. In that case absorption and emission band maxima no longer represent $S_1 \rightleftharpoons S_0$ 0–0 transition

energies but rather map the energy dependence of the Franck–Condon factor.

Another reason for inhomogeneous line broadening is spectral diffusion or relaxation due to either some slow molecular reorganization occurring even in solid matrices at low temperatures or energy transfer. In the present context only the latter process will be dealt with. In a dense ensemble an excited chromophore will be coupled to its nonexcited neighbors via multipole and exchange coupling, whichever is stronger. This leads to energy transfer and, provided that the variance of the site energy distribution is $\gg kT$, to spectral relaxation because energy transfer is a downhill process. The asymmetry of the transfer rate among the electronically coupled sites i and j renders mathematical treatment of that process difficult if not untractable in closed analytic form. An approximate solution can be obtained by employing the effective medium approach.⁵ Monte Carlo simulation⁶ has been applied as an alternative and consistent numerical method to delineate time dependent spectral relaxation. In the present context it will suffice to mention only the essential results obtained for a Gaussian-shaped density of states (DOS) appropriate for organic systems in which the density of chromophores is large enough for central limit theorem to apply as far as inhomogeneous broadening due to van der Waals coupling with the surrounding medium is concerned.⁷ Inhomogeneous absorption profiles of organic chromophores are in accord with this notion.⁸ It is less straightforward that the DOS resulting from a distribution of effective chain lengths of a conjugated polymer should be similarly shaped.

It is easy to show that a dilute noninteracting ensemble of excitations generated at an arbitrary energetic position within a Gaussian-shaped DOS of chromophores of variance σ tends to relax to a mean energy level at energy $-\sigma^2/kT$ below the center of the DOS irrespective of the coupling mechanism.⁵ The shape of the equilibrated ensemble will also be a Gaussian of the same width. However, if excitations have a finite lifetime and if $\sigma/kT \gg 1$, they will decay radiatively or nonradiatively before dynamic equilibrium is attained because the time to reach that energy increases exponentially with δ^2 ($\delta = \sigma/kT$) and may exceed their intrinsic lifetime. The slowing of relaxation as time progresses is a direct consequence of the dilution of potential acceptor states at the low-energy tail of a Gaussian-shaped DOS.⁹ Time dependent spectral relaxation can be probed experimentally by monitoring either the fluorescence spectrum of the system at different delay times after excitation by a short excitation pulse¹⁰ or the decay of the emission at different spectral positions.¹¹

The slowing of spectral relaxation within the tail of an inhomogeneously broadened absorption profile of a dense manifold of absorbers opens the possibility to do site-selective fluorescence spectroscopy (SSFS) even in optically dense media. This technique was originally developed to allow the spectra of chromophore molecules matrix-isolated in low-temperature glasses to be observed subject only to homogeneous broadening.³ It involves the

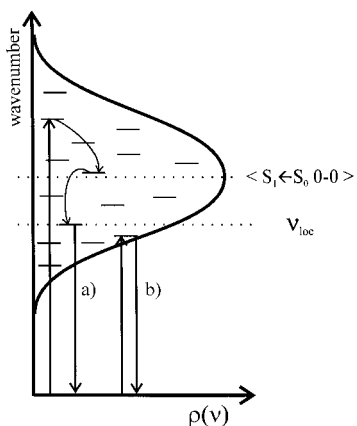


FIGURE 2. Scheme of the basic idea of site-selective spectroscopy. For excitation below the localization energy ν_{loc} any spectral migration in the density of states is missed (b). The excited site is equal to the emitting one. In contrast to this the spectral relaxation after excitation above ν_{loc} (a) destroys site selectivity.

use of a spectrally narrow laser which makes it possible to excite selected chromophores from among a large ensemble contributing to an inhomogeneously broadened absorption. Only those whose transition energy is accidentally resonant with the laser are excited, and provided that excitation is into the $S_1 \leftarrow S_0$ 0–0 line, the resulting emission spectrum is a homogeneously broadened emission that provides information on the true molecular Stokes shift and coupling to molecular vibration. One problem, however, is that stray light effects preclude measuring the $S_1 \rightarrow S_0$ 0–0 transition that would, by definition, be resonant with the laser unless $S \gg 1$. It is, therefore, not generally possible to determine the exact value of the coupling constant S because the intensity of the $S_1 \rightarrow S_0$ 0–0 transition is unknown. However, if a well-resolved pattern of sharp vibronic $S_1 \rightarrow S_0$ 0–0 modes is observed in resonantly excited SSF spectra, one can conclude that S must be on the order of 1, which is typical for rigid π -electron systems. A requirement in addition to having $S \approx 1$ for observing line-narrowed spectra is that any interchromophore interaction be vanishingly small. For reasons discussed above, this requires that upon investigating an optically dense system the excitation energy ν_{ex} be on average below a threshold ν_{loc} that separates states participating in transport from those that do not (Figure 2). Exciting at $\nu_{ex} > \nu_{loc}$ will therefore result in fluorescence spectra that are inhomogeneously broadened due to electronic energy relaxation occurring through migration of the excited states prior to their radiative decay. These spectra will be virtually independent of ν_{ex} since the emission is subsequent to the energy migration process. For $\nu_{ex} \leq \nu_{loc}$ a turnover to resonant or quasi-resonant (if a Stokes shift occurs) behavior is expected, and the spectra should show only homogeneous broadening since absorption and emission are then expected to be associated with the same chromophore. Thus, spectra recorded with excitation below ν_{loc} can allow measurement of the true Stokes shift that arises from structural relaxation after photoexcitation, unaffected by spectral diffusion effects associated with energy transfer. SSF

spectroscopy is, thus, a convenient method to differentiate among various contributions toward inhomogeneous band broadening and to provide a handle on the origin of a Stokes shift observed under conventional broad band excitation.

Site-selectively-recorded fluorescence spectra resemble gas phase spectra as far as the vibronic structure is concerned yet feature so-called phonon wings at the low-energy side of each vibronic line in addition. These result from coupling of the excited molecule to low-frequency modes of the surrounding matrix. Its intensity relative to the zero phonon line can be expressed via the Debye Waller factor.³ The homogeneous width of the zero phonon line usually reflects the dephasing time of the excitation.

The instrumentation required for site-selective fluorescence spectroscopy is a light source of spectral band width much less than the inhomogeneous absorption profile, a cryostat allowing measurements at low temperatures, preferentially near 4.2 K, where kT is much less than the inhomogeneous width σ , and a high-resolution monochromator. Both cw and pulsed lasers are suitable provided they are tunable within the spectral range of the inhomogeneously broadened $S_1 \leftarrow S_0$ 0–0 transition. In the latter case time-integrating detection techniques have to be employed for obtaining steady state spectra. On the other hand, use of a tunable subnanosecond pulsed lasers would permit analyzing the dynamics of excitation dynamics via monitoring the time evolution of fluorescence spectra by recording complete emission spectra as a function of either delay time or spectrally resolved decay patterns.

Most of the experiments referred to in the following sections were performed with a tunable dye laser of spectral band width $\sim 0.2 \text{ cm}^{-1}$ pumped by an excimer laser operated at a repetition rate of typically 10 Hz. Fluorescence light was spectrally analyzed by a Jobin Yvon U1000 double monochromator with a maximum spectral resolution of 0.2 cm^{-1} or by an optical multichannel analyzer. The detector unit of the double monochromator consisted of a cooled photomultiplier and a Boxcar averager to improve the signal to noise ratio.

3. Spontaneous Site-Selective Fluorescence

The general endeavour of the SSF spectroscopy done by the Marburg group was to obtain information on the photophysics of conjugated polymers and their related oligomers. Those systems were claimed to behave like one-dimensional semiconductors¹² rather than like more conventional π -conjugated molecules. This would imply that electron–electron interaction, e.g., Coulomb as well as correlation effects, are weak while coupling to vibrations is strong. The occurrence of a Stokes shift between absorption and emission was taken as one piece of evidence in favor of this notion. SSF spectroscopy turned out to be the method of choice to address that issue.¹³

3.1. Oligoarylenevinylene. The SSF spectra of unsubstituted oligoarylenevinylenes, OPV(1) and OPV(2),

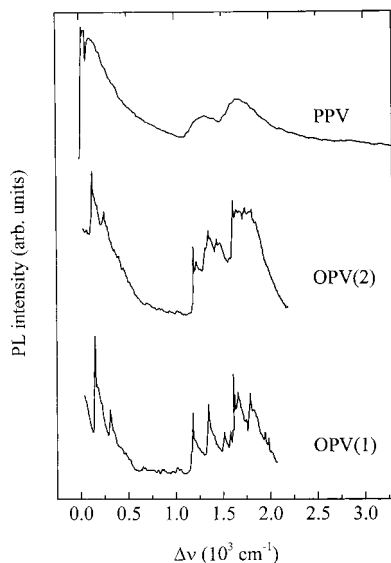


FIGURE 3. Comparison of SSF spectra of OPV(1), OPV(2), and polyphenylenevinylene (PPV).

containing three and four phenyl groups, respectively, embedded in a low-temperature (6 K) MTHF glass reveal a well-resolved vibronic structure^{14,15} (Figure 3). Zero phonon lines can be identified for vibrational energies of 160 cm^{-1} (s), 320 cm^{-1} (w), 1170 cm^{-1} (s), 1340 cm^{-1} (s), 1500 cm^{-1} (w), 1570 cm^{-1} (w), 1620 cm^{-1} , 1670 cm^{-1} (s), and 1790 cm^{-1} (s), (s) and (w) standing, respectively, for strong and weaker transitions. The spectral origin is set by the laser line implying the absence of a Stokes shift and, unfortunately, precluding determination of the intensity of the $S_1 \rightarrow S_0$ 0–0 origin because of stray light effects. Therefore, the exact value of the Huang–Rhys factor cannot be determined. However, the fact that the 0–1 fundamental vibrations rather than overtones dominate the spectrum indicates that $1 < S < 2$. A series of 6 K fluorescence spectra of a film of the associated polymer is shown in Figure 4.¹⁶ Above a certain value of ν_{ex} the spectra are invariant against changing ν_{ex} and are inhomogeneously broadened. Upon lowering ν_{ex} beyond a critical value ν_{loc} , the spectra become sharper and shift linearly with ν_{ex} . In keeping with the concept put forward in section 2, ν_{loc} is identified as the demarcation energy that separates the transition energies of polymer segments which can transfer their excitation energy to a more extended polymer segment absorbing at still lower energy from those of segments that cannot. However, in no case are sharp zero phonon features observed, indicating that a line-broadening mechanism becomes operative as the emitting segments get longer. Zero phonon lines are already absent in the five-membered OPV.¹⁷ We conjecture that this is due to some distortion of the chain segments in the ground state and its modification after excitation. In a conjugated polymer the effective conjugation length is defined as the length of a perfectly ordered finite chain whose $S_1 \rightleftharpoons S_0$ 0–0 transition energy would coincide with the measured transition energy and which is electronically decoupled from its neighbor along the same polymer strand. This is likely to be an oversimpli-

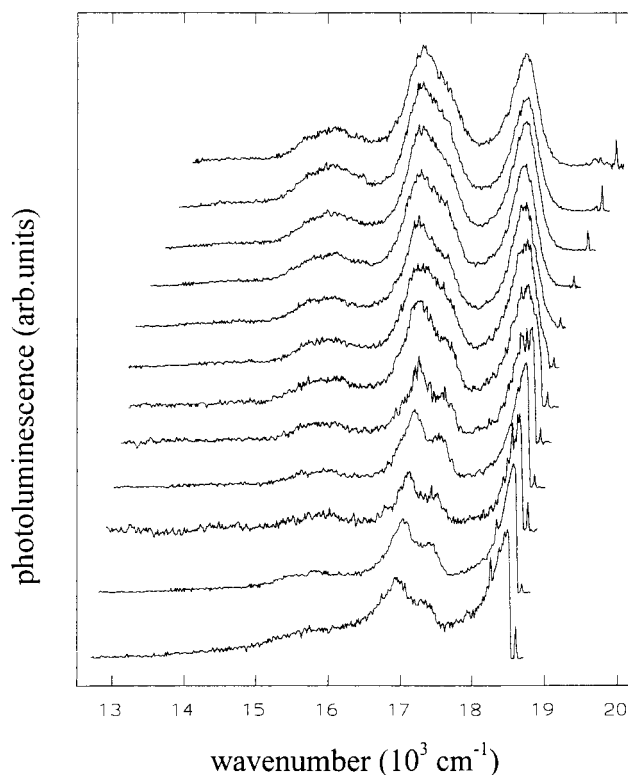


FIGURE 4. A series of fluorescence spectra of PPV parametric in excitation energy. For lower excitation energies the $S_1 \rightarrow S_0$ 0–0 band is divided into two bands. (The high-energy spike marks the laser energy.)

fication. The segment will not be perfectly ordered nor will a topological kink or twist decouple adjacent segments completely. Upon promoting a π -electron from the ground state into a higher lying state, some minor readjustment within the skeleton of the segment may occur that leads to some spectral broadening even in site-selectively-recorded spectra. This hypothesis is supported by the fact that residual line broadening is more effective the larger the inhomogeneous width of the absorption band and, concomitantly, disorder. An example is the phenyl-substituted PPV in which the bulky substituent causes the inhomogeneous band width to double as compared to PPV.¹⁵

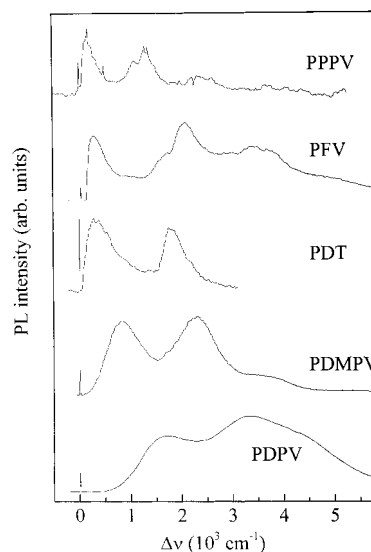
It has been of particular importance to recognize that, except for this residual line broadening, the SSF spectrum of the polymer is virtually the same as that of the oligomer (Figure 3). This indicates that molecular vibrational modes are essentially unaffected by chain elongation, a conclusion in complete agreement with the results of resonance Raman studies and theoretical calculations.^{18,19} It is further noteworthy that the intensity distribution is also very similar, indicating that the S value and, hence, the relaxation energy in the excited state are also the same for oligomer and polymer. Taking $S \approx 1.5$ and $\hbar\omega$ as an average vibrational energy yields as a rough estimate $E^{\text{rel}} \approx 0.3$ eV in good agreement with theoretical estimates.²⁰ This supports the notion that the spectroscopic properties of PPV reflect those of an ensemble of oligomers with statistically varying effective conjugation length L_{eff} . The magnitude of $\langle L_{\text{eff}} \rangle$ as well as its variance depends on

Table 1. Structural Formulas of Discussed Materials

name	abbreviation	structure formula
Oligo(phenylenevinylene)	OPV(1)	
Poly(p-phenylenevinylene)	PPV	
Poly(4,4'-biphenylene-(1,2-diphenylenevinylene))	PDPV	
Poly(2,2'-dimethyl-1,1'-biphenyl-4,4'-vinylene)	PDMPV	
Poly(2,7-fluorenylvinylene)	PFV	
Ladder-type dimer	LPP(2)	
and		
Ladder-type polymer	MeLPPP:	
1,4-Bis(p-α-cyano-styryl)-2,5-dioctyloxy-benzene	CNSB	

sample perfection which, in turn, depends on the sample preparation, e.g., stretch orientation, and interchain packing constraints imposed, for instance, by substitution.¹⁵ These results also demonstrate that it is illegitimate to attribute the Stokes shift seen in conventionally recorded fluorescence spectra of conjugated polymers to electron-phonon coupling being strong. It has, instead, to be identified with the energy an excitation loses while migrating incoherent among a distribution of chromophores with accidentally different transition energies. This concept also explains why nonresonant excited fluorescence spectra bear some bathochromic shift upon lowering the temperature.²¹ This simply reflects the temperature dependence of the electronic relaxation process rather than the freezing out of torsional modes.

There are cases, though, in which a finite Stokes shift is the manifestation of substantial molecular relaxation after excitation. Examples are PPV-like systems in which the phenyl ring is replaced by a biphenyl moiety, if modified by substitution, such as poly(4,4'-biphenylene-(1,2-biphenylene)) (PDPV), poly(2,2'-dimethyl-1,1'-biphenyl-4,4'-vinylene) (PDMPV), and poly(2,7-fluorenylvinylene) (PFV)²² (for structure formulas see Table 1). SSF spectra recorded under the premise that the emission energy shifted linearly, though non-resonantly, with the excitation energy are portrayed in Figure 5. The appearance of a Stokes shift δ , decreasing in the series PDPV, PDMPV, PFV, and PPV is obvious. Values for δ , S , and the energy of the coupling mode are listed in Table 2. That PDPV and PDMPV exhibit both the largest S values and the largest phonon energies proves that δ is related to coupling of the excited state to a torsional mode of the chain. In the ground state the structure of the biphenyl is tilted, the angle between the planes of the rings being about 20°,

**FIGURE 5.** Quasi-resonant fluorescence spectra of a series of conjugated polymers. The abscissa scale is relative to the laser energy.**Table 2. Stokes Shift δ , Huang-Rhys Factor S , and Phonon Energy $\hbar\omega_{ph}$ for conjugated Polymers**

	δ/cm^{-1}	S	$\hbar\omega_{ph}$
PPPV	~100	2–3	~20
PPV	~100	2–3	~20
PFV	~200	~3	~33
PDMPV	770	9	85
PDPV	1700	11	155
PDT	300	2	75
PDA	90	~2.5	18

while in the excited state a planar geometry is favored. This is the result of a trade-off between steric repulsion and conjugation. Upon excitation the conformation of PDPV relaxes toward a new, planar, equilibrium position, equivalent to strong coupling to a torsional mode. This assignment is supported by the decrease of $\hbar\omega_{ph}$ due to the combined effect of the increase of the moment of inertia upon adding a methyl group in the meta position and their mutual steric repulsion. The absolute magnitude of $\hbar\omega_{ph}$ is comparable to the energies of twist modes in related molecules in the gas phase, such as biphenyl ($\hbar\omega_{ph} = 70 \text{ cm}^{-1}$), benzaldehyde (110 cm^{-1}) and *p*-methylbenzaldehyde (85 cm^{-1}). Locking phenyl group motion by covalent bridging in PFV reduces δ to 200 cm^{-1} .

3.2. Oligo-*p*-phenylenes. The absorption and fluorescence spectra of unsubstituted oligo-*p*-phenylenes display only a weak bathochromic shift upon increasing the chain length²⁵ indicative of weak π -conjugation due to the ring twists. They can be planarized by the formation of covalent bonds among adjacent phenyl rings as shown by Scherf and co-workers.²⁶ This leads to improved π -conjugation, manifest in a substantial bathochromic shift of the absorption spectrum. Absorption and fluorescence spectra of the ladder-type polymer MeLPPP—present in the form of a film—are narrower than those of any other noncrystalline conjugated polymer and feature only a small Stokes shift (Figure 6). This is due to the rigidity of the backbone that favors intra- as well as interchain ordering.²⁷

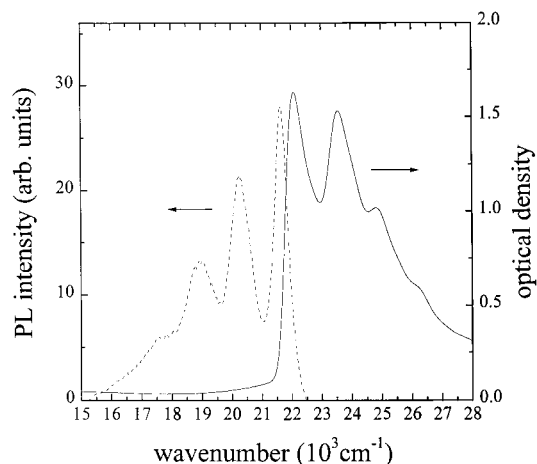


FIGURE 6. Absorption and photoluminescence spectra of a MeLPPP film at 295 K.

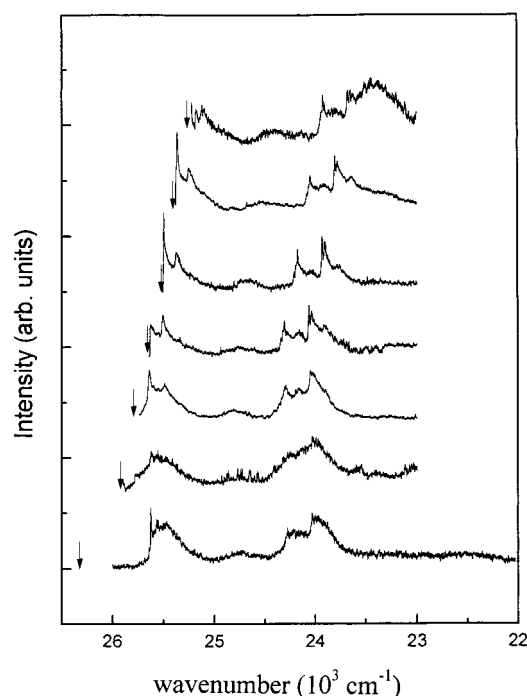


FIGURE 7. A series of fluorescence spectra of the LPP dimer embedded in a MTHF matrix at 6 K. The concentration was 10^{-5} M. The arrow indicates the excitation energy.

A series of SSF spectra recorded with the LPP dimer dispersed in MTHF glass at 6 K is shown in Figure 7. It reveals a set of vibronic bands each consisting of a sharp 0–0 feature followed by a phonon wing. There is a noteworthy feature associated with the bottom spectrum of Figure 7. Usually site selectivity is eroded upon exciting into a vibronic $S_1 \leftarrow S_0$ $n \leftarrow 0$ band because chromophores of different electronic origin are excited via different combinations of vibrational and phonon modes that couple to the $S_1 \leftarrow S_0$ origin. An exception of that rule occurs if inhomogeneous broadening as well as coupling to lattice modes is weak and if excitation occurs in a range in which only a single vibrational mode is active. In that case emission retains its line-narrowed character and, importantly, contains the $S_1 \rightarrow S_0$ 0–0 origin band required for an assessment of the Huang–Rhys factor as well as of

Table 3. Comparison of the Energies (cm^{-1}) of the Dominant Vibrational Modes Coupling to the Ground State of Matrix-Isolated LPP Oligomers¹⁷ and to the S_0 State of MeLPPP²⁸

monomer	LPP		MeLPPP polymer
	dimer	trimer	
175	145	120	120
260			
710			
780			
1370	1350	1320	1326
1483	1490		
1640	1620	1600	1575
			1607

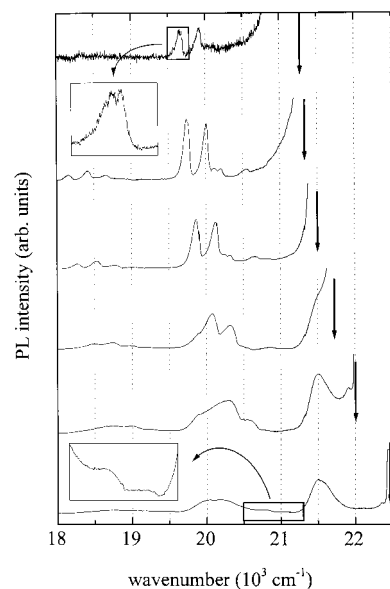


FIGURE 8. Site-selective fluorescence spectra of MeLPPP embedded in a MTHF matrix at 10 K. The arrows indicate the excitation energy. The bottom inset shows the weak quasi-resonant features on an enlarged scale. The two spectral features are identified as quasi-resonant vibrational emissions.

the relaxation energy in the excited state according to eq 5. $E^{\text{rel}} = 3900 \text{ cm}^{-1}$ is obtained. This documents that a significant displacement of the configurational coordinate is occurring upon excitation despite the rigidity of the molecular structure. It turns out that the intensity of the vibronic bands decreases somewhat with oligomer length. This indicates that S values and, concomitantly, relaxation energies decrease as the π -conjugation system gets longer. That decrease of S is an expected result which reflects the increasing delocalization of the excited state wave function. Another manifestation of the excited state becoming more spread out is the decrease of the vibrational energies with increasing oligomer length (Table 3).

The fluorescence of a methyl-substituted ladder polymer (MeLPPP) dispersed in MTHF glass recorded at 10 K reveals an inhomogeneously broadened origin band centered at $21\,500 \text{ cm}^{-1}$ with a fwhm of $\sim 300 \text{ cm}^{-1}$ followed by the vibronic features (Figure 8).²⁸ Except for weak vibronic satellites (see bottom inset in Figure 8) that appear at the high-energy side of the main vibrational features and shift with ν_{ex} while growing in intensity as ν_{ex} decreases, the emission remains spectrally invariant

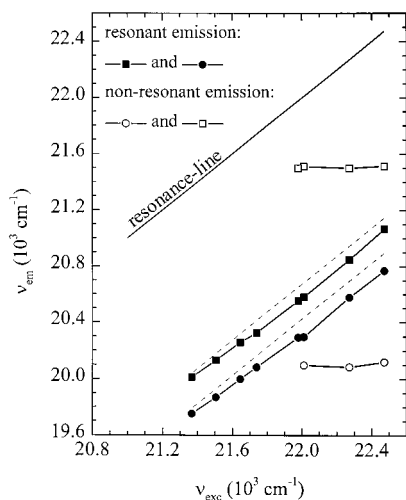


FIGURE 9. Energy of the dominant vibrational features in the fluorescence spectra of MeLPPP in MTHF as a function of the excitation energy.

upon excitation at $\nu \geq 21\,700\text{ cm}^{-1}$. The former emission is due to excitations that decay radiatively before transferring their energy to a lower energy site. For $\nu \leq 21\,700\text{ cm}^{-1}$ the dominant vibrational feature splits into a doublet and shifts with ν_{exc} (Figure 9). This is accompanied with some spectral narrowing. From the uppermost spectrum of Figure 8 it is evident that the low-energy feature is in fact a doublet as expected on the basis of the oligomer spectra.

3.3. Intra- versus Intermolecular Relaxation. A red shift of the fluorescence spectrum of a bulk sample relative to its absorption spectrum can also be a signature of intra- as well as intermolecular relaxation. A prominent example of the latter process is excimer formation in systems like crystalline pyrene or in polymers containing carbazole as a chromophore.²⁹ Excimer formation has also been invoked in relation to conjugated polymers.^{30–32} Because the spatial extension of the wave function of an excited singlet state may be comparable to the intermolecular separation, it may happen that an excimeric excitation is energetically stabilized against an on-chain excitation although the latter would initially be generated because of its higher oscillator strength.³³ Chemical substitution that favors coplanar arrangement of adjacent chains should support excimer formation. Harrison et al.³⁴ conducted a SSF study of a series of alkoxy- and cyano-substituted PPV-derivatives including unsubstituted PPV. While the spectra reported for MEH-PPV were essentially in accord with the known spectra of PPV, a PPV carrying two dihexyloxy groups at every phenylene ring and one cyano group at the vinylene group and a PPV carrying dodecyloxy and bromine functionalities at the phenylene group behaved differently. The emission energy varied sublinearly with the excitation energy, and there was a significant Stokes shift (0.25–0.3 eV) even upon excitation at the absorption tail. A plausible explanation for this was given in terms of excimer formation. In that case the dependence of the emission energy on excitation should differ from that expected for a nonexcimeric system

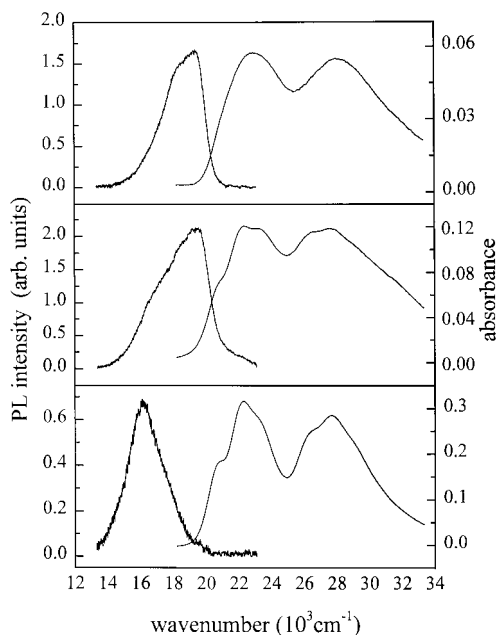


FIGURE 10. Absorption and emission spectra of (top) 20, (middle) 50, and (bottom) 80% CNSB in polystyrol at $T = 295\text{ K}$.

because excimer formation affects or may even prevent energy migration.

To conclusively separate inter- from intramolecular relaxation, SSF experiments were performed on an oligomeric member of the phenylenevinylene family, carrying a pair of cyano groups at the vinylene group and dioctyl groups at the phenylene moiety (CNSB) that could be doped into a MTHF glass at low concentration and blended with polystyrene at an arbitrary mixing ratio.³⁵ Figure 10 shows the absorption and fluorescence spectra of CNSB/PS films containing 20%, 50%, and 80% CNSB (by weight), respectively. The former become somewhat narrower as the concentration increases while the latter bear out a significant red shift. In order to differentiate between the contributions of exciton migration toward lower energy sites on the one hand and molecular relaxation on the other hand to spectral broadening, site-selective fluorescence spectra were recorded with a diluted solution ($c = 10^{-4}\text{ mol/L}$) of CNSB in MTHF at 5 K. The result, presented in Figure 11, indicates that in no case sharp spectra with zero phonon lines are observed. The energy gap between the laser energy and the center of the high-emission feature (i.e., the Stokes shift) narrows as the excitation energy is scanned toward lower energies until below a certain threshold energy quasi-resonant spectra featuring a Stokes shift of 400 cm^{-1} are observed (Figure 12). Importantly, no change in the fluorescence spectra of the 80% CNSB film is observed upon varying ν_{exc} from $32\,468$ to $20\,000\text{ cm}^{-1}$.

Observing a finite Stokes shift with the matrix-isolated molecule indicates that the CNSB molecule suffers some intramolecular relaxation after excitation. This is in contrast to an unsubstituted oligo-*p*-phenylenevinylene counterpart molecule (see section 3.1) and indicates that it is the presence of the substituents that opens a pathway for structural relaxation. This is likely to be due to some

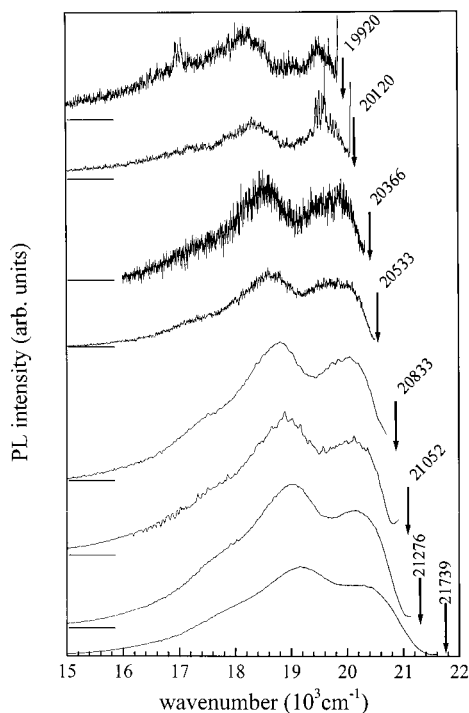


FIGURE 11. A series of fluorescence spectra of CNSB in a MTHF matrix ($c = 10^{-4}$ mol/L) at 5 K parametric in excitation energy. The latter is given in wavenumbers and marked by arrows.

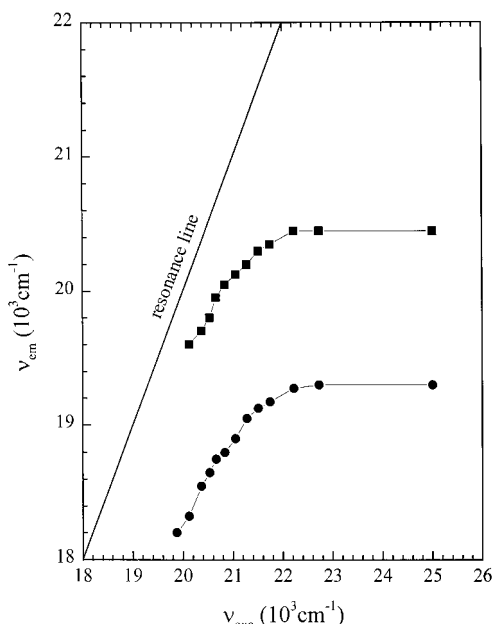


FIGURE 12. Energy of the $S_1 \rightarrow S_0$ 0–0 (squares) and $S_1 \rightarrow S_0$ 0–1 (circles) emission as a function of the excitation energy.

rotational freedom of the substituents about their single bonds in conjunction with some charge localization at the donor/acceptor functionalities.

The emission spectrum of the solid film containing 20% CNSB excited well above the absorption edge is virtually the same as that of the isolated molecule except for a bathochromic shift by about 1000 cm^{-1} . With increasing concentration a new, broad emission band centered near 16000 cm^{-1} appears. In the 80% sample it carries most of the intensity. These results correlate qualitatively with

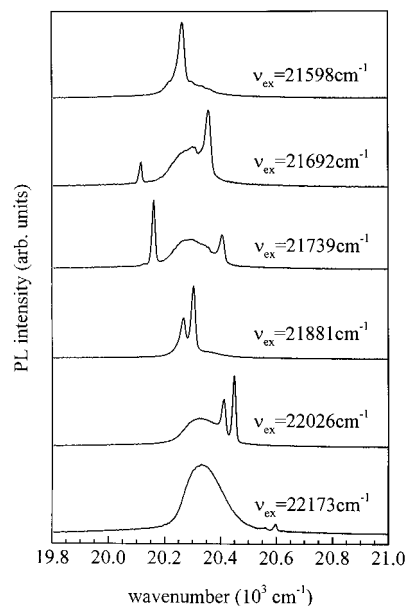


FIGURE 13. A series of fluorescence spectra of a MeLPPP film restricted to the spectral region of the $S_1 \rightarrow S_0$ 0–1 band ($T = 295$ K). The intensity of the sharp features maps the spectral overlap with the $S_1 \rightarrow S_0$ 0–1 emission.

those of Harrison et al.³⁴ on films of the polymer analog of CNSB carrying hexyloxy—instead of octyloxy—groups except that the 5 K spectra of CNSB do not exhibit any vibronic features. Since no aggregate-specific absorption is detectable, the broad emission band from the 80% sample has been assigned to an excimer. On the basis of the present steady state measurement we cannot decide conclusively if essentially all sites are capable of excimer formation, such as, e.g., in a pyrene crystal, or if energy transfer toward incipient dimers is involved as in polyvinylcarbazol.^{36,29} The fact that no spectral changes are observed upon exciting low-energy tails from which energy transfer at 5 K is hardly possible is suggestive of the former option, though.

4. Amplified Spontaneous Emission under SSF Conditions

Site-selective fluorescence spectra of a MeLPPP film reveal an interesting phenomenon. While the conventional emission spectrum is observed upon high-energy excitation, i.e., $\nu_{\text{ex}} \geq 22000 \text{ cm}^{-1}$, sharp features appear superimposed onto the nonresonant first (cumulative) vibronic feature as ν_{ex} enters the spectral range of the inhomogeneously broadened $S_1 \rightarrow S_0$ 0–0 emission band. They are shifted from the laser line by 1326 and 1575 cm^{-1} , respectively. Their relative intensities change with ν_{ex} , obviously mapping their spectral overlap with the underlying nonresonant vibronic emission feature (Figure 13). Their absolute intensity grows superlinearly with excitation dose (inset of Figure 14). The lineshape of the sharp features can best be described by a Gaussian profile; the line width is almost temperature independent, fwhm values being 7.1 cm^{-1} (6 K), 8.8 cm^{-1} (77 K), and 9.0 cm^{-1} (295 K). Figure 14 demonstrates that appearance of the

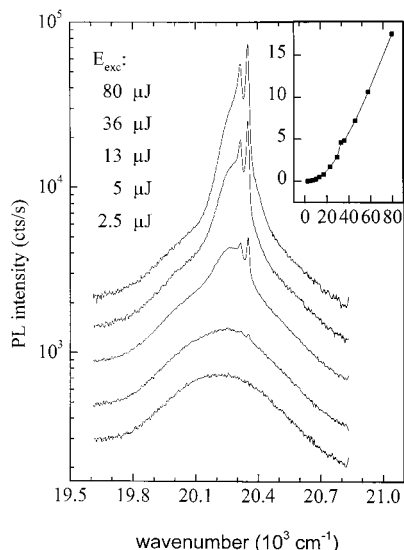


FIGURE 14. $S_1 \rightarrow S_0$ 0–1 band of a MeLPPP film for various energies of the pump pulse ($\nu_{\text{ex}} = 21\,928\text{ cm}^{-1}$, $T = 77\text{ K}$). Note the logarithmic ordinate scale. Inset: dependence of the intensity of the superimposed sharp emission feature on the energy of the pump pulse.

sharp features is accompanied by another spectral feature, about 200 cm^{-1} broad, that grows on top of the broad vibronic band and becomes narrower with increasing pump power. Side face detection of the emission demonstrates that wave-guiding effects are important.

Comparing the energy offsets of the narrower emission features from the laser line with the energies of the dominant skeleton vibrations of LPPP oligomers (Table 3) confirms that these are vibronic satellites associated with an emission that is resonant with excitation taking into account the decrease of the vibrational energies with increasing chain length (see above). The $\sim 180\text{ cm}^{-1}$ broad emission feature has been attributed to amplified spontaneous emission (ASE). Evidence for this assignment comes from the fact that a critical threshold pump energy per pulse is required and from pump and probe experiments.^{37,38} The latter bear out an increase in transmission in the spectral range where the sample emits rather than absorbs. The gain mechanism must be the same as the one involved in a conventional dye laser.

Upon exciting at the low-energy side of the absorption band some of the initially excited chromophores will have a sufficiently close neighbor with lower lying energy level to which the excitation can be transferred nonradiatively by Förster transfer while others will not. The percentage of the latter increases as ν_{ex} is scanned across ν_{loc} . Therefore, the fluorescence spectrum emitted at $\nu_{\text{ex}} \geq \nu_{\text{loc}}$ will carry a resonant and a nonresonant contribution as evidenced by Figure 8. If the density of excited states exceeds the critical value for stimulated emission to become important, an ASE emission evolves that originates from relaxed excited states under the constraint of some spectral narrowing, reflecting the quality of the resonator. That inhomogeneously broadened ASE will, however, also stimulate those excitations to emit that are still localized at their parent site and vice versa is sup-

ported by the fact that the variation of the intensity of the sharp features maps the intensity profile of the inhomogeneously ASE feature related to the $S_1 \rightarrow S_0$ 0–1 transition (Figure 13). Upon shifting ν_{ex} from the absorption maximum toward ν_{loc} , the 1575 cm^{-1} vibronic line appears first and is dominant as long as it overlaps with the ASE mode. Subsequently, the 1326 cm^{-1} line takes over. The effect vanishes upon scanning ν_{ex} significantly below ν_{loc} . In that case neither is there a sufficiently large population of spectrally relaxed S_1 excitations available for stimulated emission nor is the total density of excitations sufficient to establish gain. Further unambiguous proof that the sharp features are due to nonrelaxed excitations is that they are offset from the laser line by vibrational energies only. In passing we note that the resonant character of that emission testifies that no self-trapping of the excited state occurs, which had been discussed previously in relation to polydiacetylenes.³⁹

5. Conclusion

The above examples illustrate the usefulness of site-selective fluorescence spectroscopy to remove inhomogeneity effects in the emission spectra of π -conjugated organic molecules and polymers. The method is more versatile than hole-burning spectroscopy and easier to implement experimentally. Site labeling is done solely by selecting a group of absorbers via their accidentally identical transition energies and does not require any subsequent photophysical or photochemical transformation as does hole-burning spectroscopy, nor does it require the homogeneous line widths of the chromophores to be extremely narrow. Operating on a time scale set by the lifetime of the excited state, it is unable to probe slow reorganization processes, leading to spectral diffusion. Another problem is that stray light effects usually preclude detection of $S_0 \rightarrow S_1$ 0–0 zero phonon lines. The method is appropriate to eliminate spectral broadening and to determine fluorescence spectra of individual chromophores required for vibrational analysis. It also allows various sources of inhomogeneous broadening of conventionally recorded spectra to be distinguished, in particular to separate spectral shifts due to conformational changes of a chromophore after excitation from those that arise from energy transfer. Inter- and intramolecular pathways leading to structural relaxation can be unraveled by concentration dependent studies. It has further been demonstrated that under appropriate excitation densities stimulated emission can be observed under resonant excitation conditions.

We thank V. Brandl, S. Heun, R. F. Mahrt, and T. Pauck for their contributions to this work. Samples were kindly provided by D. D. C. Bradley, W. Heitz, U. Scherf, and K. Müllen. Financial support from the Stiftung Volkswagenwerk and the Fond der Chemischen Industrie is gratefully acknowledged.

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AR960228K