How Chromophore Shape Determines the Spectroscopy of Phenylene−Vinylenes: Origin of Spectral Broadening in the Absence of Aggregation

K. Becker,[†] E. Da Como,*,[†] J. Feldmann,[†] F. Scheliga,[‡] E. Thorn Csányi,[‡] S. Tretiak,[§] and J. M. Lupton*,[∥]

Photonics and Optoelectronics Group, Physics Department and CeNS, Ludwig-Maximilians-Universität, Amalienstr. 54, 80799 München, Germany, Institute for Technical and Macromolecular Chemistry, Universität Hamburg, 20146 Hamburg, Germany, Theoretical Division and Center for Integrated Nanotechnologies (CINT), Los Alamos National Laboratory (LANL), Los Alamos, New Mexico 87545, and Department of Physics, University of Utah, Salt Lake City, Utah 84112

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Single oligo(phenylene-vinylene) molecules constitute model systems of chromophores in disordered conjugated polymers and can elucidate how the actual *conformation* of an individual chromophore, rather than that of an overall polymer chain, controls its photophysics. Single oligomers and polymer chains display the same range of spectral properties. Even heptamers support π-electron conjugation across ∼80° curvature, as revealed by the polarization anisotropy in excitation and supported by quantum chemical calculations. As the chain becomes more deformed, the spectral linewidth at low temperatures, often interpreted as a sign of aggregation, increases up to 30-fold due to a reduction in photophysical stability of the molecule and an increase in random spectral fluctuations. The conclusions aid the interpretation of results from single-chain Stark spectroscopy in which large static dipoles were only observed in the case of narrow transition lines. These narrow transitions originate from extended chromophores in which the dipoles induced by backbone substituents do not cancel out. Chromophores in conjugated polymers are often thought of as individual linear transition dipoles, the sum of which make up the polymer's optical properties. Our results demonstrate that, at least for phenylene−vinylenes, it is the actual shape of the individual chromophore rather than the overall chromophoric arrangement and form of the polymer chain that dominates the spectroscopic properties.

Molecular-level engineering in plastic electronics requires a precise understanding of how a particular physical or chemical structure impacts on the physical properties of the material. Disorder effects on the ensemble level can often mask the subtle interplay between function and structure. Large macromolecules such as conjugated polymers are particularly prone to energetic disorder, which gives rise to substantial spectral broadening and is generally attributed to a "*particle in a box*"-like picture of varying chromophore lengths.[1] Disorder effects have commonly been investigated in matrix isolated materials, such as polyenes, where subtle interplays between molecular shape and electronic structure have been identified.[2−5] However, matrix isolation on its own is not sufficient to overcome disorder but merely helps to screen intermolecular effects. The intrinsic molecular properties themselves are accessible with single-molecule spectroscopy. Although this technique helps to overcome the ensemble limitations, a single polymer chain can still contain many chromophores.[6−12] Energy transfer between these chromophores can mask the true photophysics of the individual spectroscopic unit. Although polarization-resolved spectroscopy has

yielded detailed insight into the conformation of the polymer *chain*,[7,8,11,13−15] very little is known about the shape of the *individual chromophore*. Because a physical bend can potentially interrupt the π-electron conjugation, the chromophore is generally thought to be linearly extended in space leading to linearly polarized absorption.[8,16] However, building on the earlier realization that isolated polyphenyls may be able to adopt nonplanar conformations,[17] recent quantum chemical studies,[18] along with ultrafast luminescence[19] have suggested that the individual chromophore itself may support a certain degree of bending, thus inducing polarization loss without sacrificing π-electron delocalization.

In this letter we report single-molecule spectroscopy of large oligomers of 2,5-di(2′-ethylhexyloxy)-1,4-phenylene-vinylene) (DEH-PV, structures given in Figure 2) and compare these results to measurements of the structurally related highly disordered model polymer poly(2-methoxy-5-(2′-ethyl-hexyl-oxy)-1,4-phenylene-vinylene) (MEH-PPV). A wide range of spectroscopic properties, previously associated with interchromophoric interactions, are observed in the isolated chromophore.[9,20,21] Remarkably, the fluorescence linewidth correlates with polarization anisotropy, which provides a direct measure of chromophore conformation. In agreement with recent investigations of the twisting of single biphenyl units,[22] we find that even the shortest oligomers (7mers) can support a curvature of
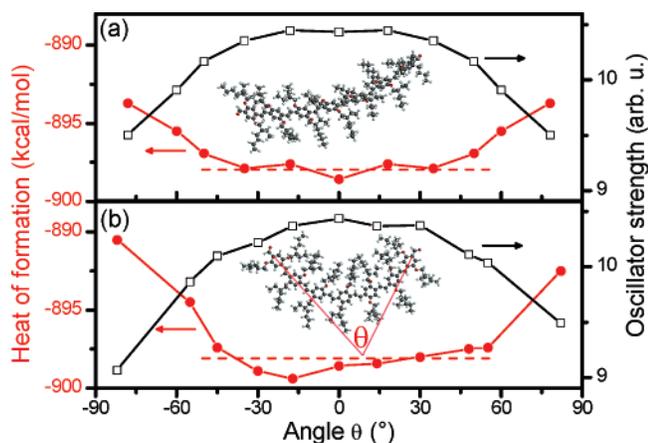
* Corresponding authors. E-mail: enrico.dacomo@physik.uni-muenchen.de; lupton@physics.utah.edu.
† Ludwig-Maximilians-Universität.
‡ Universität Hamburg.
§ Los Alamos National Laboratory.
∥ University of Utah.

Figure 1. Thermodynamically viable conformations of a phenylene−vinylene heptamer, the model system of an MEH-PPV chromophore. The calculated heat of formation and oscillator strength of the oligomer are shown as a function of bending angle (a) out of the plane of conjugation; (b) in plane. The dashed lines indicate room-temperature thermal energy above the $\theta = 0°$ conformation. The oligomer can bend by over 50° in either direction without loss of conjugation and oscillator strength.
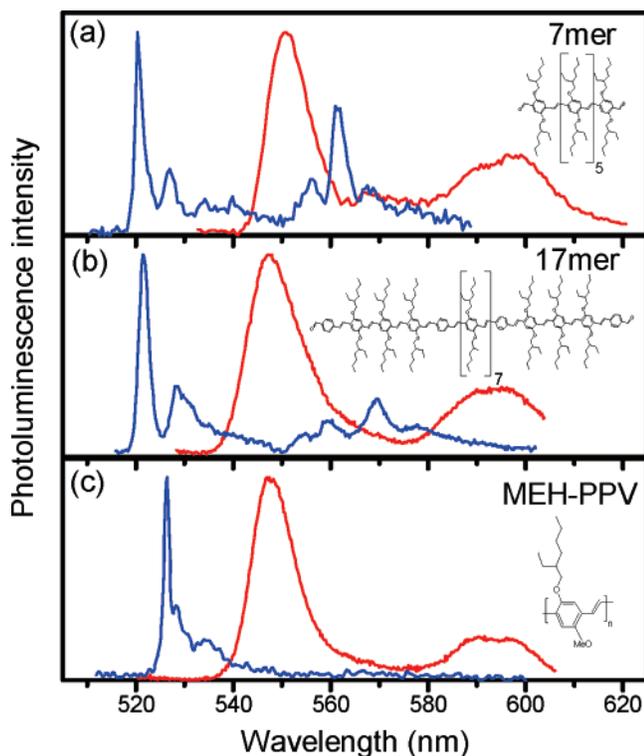
Figure 2. Examples of single chromophore luminescence spectra of six single phenylene−vinylene chains recorded at different spots (displaying narrow/broad spectra) on the three samples at 5 K. (a) OPV 7mer, (b) OPV 17mer, (c) MEH-PPV. Oligomers and polymers display essentially the same spectral features, demonstrating that the oligomers can indeed serve as models of polymer chromophores.

up to ∼80° without loss of conjugation. The spectral properties of the chromophore and thus of the polymer chain are strongly influenced by the chromophore *shape* rather than being solely controlled by its *size*. Most importantly, the emission becomes more stable for straight chromophores, an observation clearly relevant to device operation.

A conjugated polymer chain is generally thought to experience spatial disruptions to the π-electron system, leading to the formation of discrete chromophoric units on the chain. These chromophores constitute the fundamental units of the macromolecule responsible for emission and absorption. Measurements of the polarization anisotropy in excitation of a single polymer chain can provide insight into the spatial arrangement of the chromophores on the chain,[8] assuming that the absorption transition dipole lies along the chromophore long axis.[16,23] In order to assess the actual shape of the individual chromophores, we employ suitable oligomeric model systems with optical properties virtually identical to those of the polymer. Oligomers ensure that emission and absorption occur from the same chromophore without intramolecular interchromophoric energy transfer contributing to depolarization.[7,8,11,13−15] Figure 1 summarizes quantum chemical molecular dynamics calculations of a DEH-PV heptamer, which serves us as a model of an MEH-PPV chromophore. The calculations follow the previously reported excited-state molecular dynamics procedure.[24] To assess a particular bending angle θ, we enforce a molecular distortion by fixing the positions of the outermost atoms, optimize this constrained geometry, and compute the according heat of formation at optimal constrained geometry. This approach enables us to link theory to experiment: the molecules in the experiment are inevitably dispersed in a matrix and experience external forces that are not accounted for in a structure geometry optimized *in vacuo*. Figure 1a plots the calculated heat of formation and oscillator strength of the π system as a function of bending angle of the chain out of the plane. The dashed line indicates the thermal energy at room temperature relative to the stretched conformation. Distortions of up to 50° are thermodynamically viable without having to invoke additional external forces, which may potentially be exerted by the matrix. The distortions only have a minimal effect on conjugation of the system, as determined by the oscillator strength of the transition and the spatial delocalization of the respective transition density (not shown).[24] Similar distortions are possible for chain bending within the plane (panel b). Because the oscillator strength is not affected significantly, we expect to observe equally bright molecules with different degrees of polarization anisotropy in excitation.

We performed low-temperature (5 K) single-molecule spectroscopy on well-defined *para*-phenylene−vinylene oligomers (OPVs) of 7 and 17 repeat units. Mass spectrometry confirmed the monodispersity of the samples and agreed with the calculated molecular weights. Nuclear magnetic resonance spectroscopy revealed that the chains are generally in the all-trans configuration in solution, as sketched in Figure 2. We cannot exclude at the present stage, however, that a trapping of cisoid isomers occurs in the solid state. All monomers are uniformly alkyloxy-substituted in the 2,5 position of the benzene ring, but a considerable stereoirregularity is to be expected due to the possibility of the alkyl side chains rotating about the oxygen atom. Samples were prepared by dissolving the compounds in toluene at concentrations of 10^{-11} M, adding Zeonex as a host polymer matrix, and spin-coating the solutions on top of SiO_2-covered silicon wafers to yield films 30 nm thick. The samples were prepared in a dry nitrogen glovebox to minimize any potential influence of oxygen or moisture on the molecular conformation[7−8,11] and subsequently mounted in a helium cold finger microscope cryostat under a vacuum of 10^{-6} mbar and studied using an epifluorescence microscope described elsewhere.[9] Luminescence was excited by an Ar^+ laser (488 nm, up to 200 W/cm² intensity) and detected in 10 s integration windows. The spectra of single chains were recorded from almost diffraction-limited spots of approximately 1 μm in diameter.

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Figure 2a illustrates examples of spectra measured for two single heptamer molecules (located at different substrate spots). One spectrum is narrow (∼3 meV peak width) and peaks at 520 nm, whereas the other spectrum is much broader (∼80 meV width), peaking further in the red at 550 nm. We typically observe that the narrower spectra occur at shorter wavelengths. Virtually identical spectral features are observed for single chains of the 17mer model compound, shown in panel b. Panel c displays exemplary spectra for single MEH-PPV chains, in agreement with prior reports.[9-10] In summary, the spectra of all three materials span the same characteristics over a range of 505−595 nm, the only subtle difference being a slight increase in vibronic intensity due to stronger electron−phonon coupling in the less delocalized oligomeric systems.[25] The spectral similarity of oligomers and polymers demonstrates that the heptamer is indeed a suitable model system to study the *conformation* of chromophores in MEH-PPV. We previously linked the broadened spectral features to self-aggregation of multiple chromophores on a single chain,[9,26] following well-established assignments from ensemble spectroscopy.[20,21] The fact that equal spectral signatures are observed in short oligomers and long polymer chains, however, illustrates that spectral broadening in the single chain emission *cannot be due to interchromophoric contacts*.

The possibility of intermolecular aggregation or dimerization occurring in the oligomers and giving rise to spectral broadening can be readily excluded as single-step photobleaching is observed, illustrating that only one molecule is present in the measurement spot at a time. In addition, the low concentration of molecules employed makes intermolecular aggregation extremely improbable. Because the transition energy of the OPV series does not converge to that of the polymer for units shorter than the hexamer,[24,27] we note that within our experimental conditions (488 nm excitation) it is not possible to excite a self-aggregate of two chromophores (e.g., two trimers) within a single heptamer; anything shorter than a hexamer would absorb at a wavelength shorter than the laser wavelength. We therefore conclude that the broad emission bands observed cannot be due to aggregation but are rather *intrinsic to the single chromophore*. The subsequent experiments address the origin of this monomolecular broadening phenomenon.

Direct information on the molecular conformation is available from measurements of the polarization anisotropy in excitation.[8] We find that the emission of the single oligomers is generally linearly polarized (34 single heptamers gave an average polarization anisotropy $\langle M \rangle = 0.93$), suggesting the involvement of one single linear transition dipole arising from the self-trapped exciton.[24] In contrast, the excitation, which is probed by rotating the laser polarization by a $\lambda/2$ plate and monitoring the PL intensity, indicates a departure from a linear absorbing unit for many single oligomer chains, in agreement with recent reports that even single *para*-phenylene dimers can undergo substantial bending and twisting.[22] This difference between absorption and emission anisotropy arises because absorption probes a larger region of the molecule than emission, where self-trapping of the exciton due to structural relaxation reduces the number of repeat units involved in the electronic excitation.[24] Following from Figure 1, a spatial distortion of the chain will induce a low polarization anisotropy in absorption without affecting the oscillator strength of the transition. Emission will occur due to a transition involving fewer monomer units following exciton self-trapping[24] and will therefore tend to display a higher degree of polarization.

Following ref 8, the emission intensity $I(\alpha)$ was recorded for a minimum of two complete rotations of the angle of laser polarization α and is described accurately by the relation $I(\alpha) \propto 1 + M \cos 2(\alpha - \phi)$, where M constitutes the polarization anisotropy and ϕ the phase angle of each individual molecule. $M = 1$ denotes a fully extended chain, whereas $M = 0$ corresponds to a molecule that can absorb light of all polarizations and is therefore strongly deformed. Because a single oligomer should give rise to precisely one dipole transition in emission, M is independent of emission wavelength and we therefore integrate intensity over the entire spectral region of emission. We studied the 7mer to ensure that the chain contains exactly one chromophore. Surprisingly, we find that the polarization anisotropy correlates directly with the transition linewidth as shown in Figure 3a. The narrow spectral features correspond to the most extended oligomers, while the broad spectra originate from bent units. In contrast to the case of MEH-PPV,[8] a histogram of the polarization anisotropy (not shown) indicates that there is no apparent preferential conformation the oligomer will take: the values scatter evenly so that no distinct species can be identified. We note that the lowest polarization anisotropies ($M \rightarrow 0.1$) suggest that the oligomer is bent by almost 80°. At the same time, the conjugation is not disrupted because this would lead to a dramatic shortening of the exciton confinement length with the associated blue shift and reduction in oscillator strength seen in shorter oligomers.[27] These observations are in agreement with our theoretical modeling (Figure 1), which suggests the occurrence of chain bending without strong modification of the total molecular energy and the transition oscillator strength.

It is not immediately obvious how a molecular distortion impacts the transition energy. At first glance, a simple *particle in a box* picture would appear to imply that increased distortion of the exciton's confinement potential should lead to a blue-shift of the emission. Such a shift can be reproduced by calculations; however, the molecular relaxation energy (the Stokes' shift) is also affected by distortion. In addition, we recently demonstrated that the MEH-PPV emission is strongly affected by the polarity of the local environment.[28] This effect is observed both in ensemble solvatochromism as well as in the single chain Stark shift.[28] Depending on the overall chain conformation, the transition energy of molecules embedded in a matrix can be strongly modified by local microscopic electric fields resulting from a polarization of the immediate environment.[28] At present, it is neither possible nor meaningful to predict all influences of the environment and the molecular shape on transition energy. The experiment, however, draws a clear picture: the OPVs exhibit a spectral *red shift* with increasing chain distortion. Figure 3b shows a plot of the transition linewidth (which depends on polarization anisotropy) against the peak position of the oligomer zero-phonon line. The more stretched the oligomer is ($M \rightarrow 1$), the further in the blue the emission occurs. Again, the transition is smooth, and no distinct species can be identified. Although the 17mer on average tended to lower polarization anisotropies, that is, a higher probability of bending due to the greater length, we observed a qualitatively similar correlation between linewidth, peak position, and anisotropy (not shown).

Further evidence for the correlation of linewidth with shape comes from single-molecule Stark spectroscopy: only the narrow and not the broad spectral features of the polymer exhibit a significant linear Stark effect,[28] arising from large static dipoles (>15 D) oriented orthogonal to the backbone. This observation suggests that the static dipoles responsible for the Stark effect,
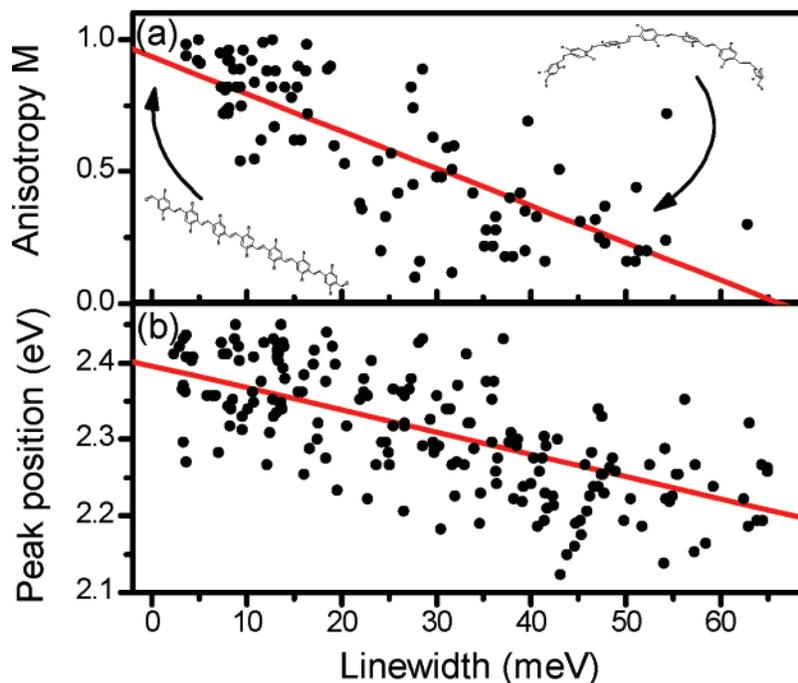
Figure 3. Conformational control of 7mer photophysics at 5 K. (a) Correlation between the 0−0 transition linewidth and polarization anisotropy in *excitation* for 98 molecules. (b) Correlation between peak position and linewidth for 191 molecules.

which are most likely induced by the methoxy sidegroups,[28] cancel out in chromophores with spectrally broad emission. A possible route for such a cancellation of dipoles lies in the chromophore collapsing into a more isotropic structure, while maintaining full conjugation. We anticipate that more elongated chromophores will also adopt a more planar geometry, with all dipole-inducing side groups aligned in parallel, thereby leading to a large collective static dipole amplifying the linear Stark shift.

If aggregation is not responsible for spectral broadening of the single emitter, then the two remaining physical origins are ultrafast electronic dephasing and spectral diffusion (i.e., a meandering of the maximum emission wavelength). Although electronic dephasing, which could conceivably depend on shape, was originally thought to be extremely fast in PPVs,[29] more recent single-molecule measurements have lowered the estimate of the homogeneous linewidth dramatically.[10] Alternatively, spectral diffusion occurs in all non-resonantly driven systems as excess excitation energy is dissipated through slight conformational rearrangements of the molecule and the surrounding matrix following excitation.[30] The more rigid a molecule and its environment, the fewer configurational degrees of freedom exist and consequently the lower the overall influence of temporal spectral dynamics on the emission. Well-known examples of this effect include the emission of single perylene molecules in glassy and crystalline matrices, where the latter case leads to orders of magnitude reduction in linewidth;[30] and the transition from disordered glassy to ordered β-phase polyfluorene,[31,32] where the latter displays improved photophysical stability and reduced spectral jitter. Because the measurement of a luminescence spectrum typically requires several seconds, spectral diffusion leads to an averaging over a range of different emission patterns of the molecule, thereby inducing effective spectral broadening.[30] One way to test this origin of spectral broadening is to study spectral fluctuations on longer time scales and extrapolate to shorter, experimentally inaccessible timescales.[9]
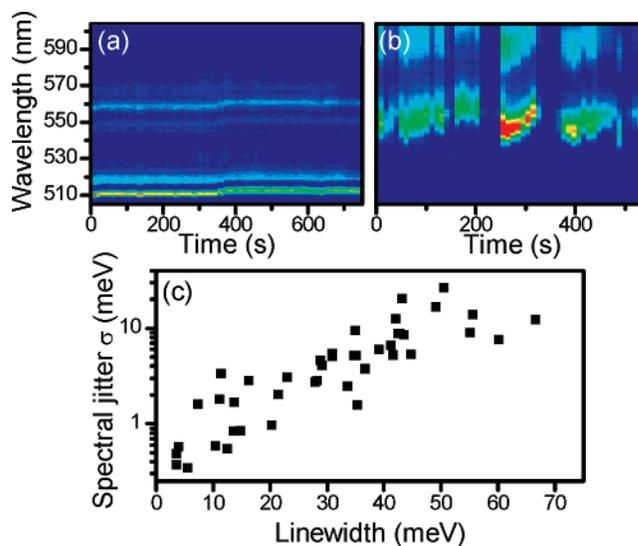
Figure 4. Influence of molecular shape and transition linewidth on the temporal stability of 17mer emission at 5 K; (a) narrow spectrum (elongated chromophore), (b) broad spectrum (bent chromophore). (c) Spectral jitter versus linewidth (bending) for 43 single chains.

Room-temperature single-molecule imaging of OPVs recently demonstrated that blinking increases in bent molecules with low excitation polarization anisotropy.[33] We confirm this observation and generalize it to the overall spectral dynamics. Figure 4a and b shows two example fluorescence traces of single 17mers. The narrow emitting species (a) is rather stable with time and shows only minimal spectral fluctuations. In contrast, the broad emitting species (b) exhibits increased spectral jumps and blinking. In order to quantify the spectral dynamics, we plot the standard deviation σ of the spectral jump from one spectrum to the next (the spectral jitter) in dependence of the linewidth (and thus molecular shape). This is shown in Figure 4c for a total of 43 17mer time traces. The jitter rises strongly with linewidth, demonstrating that spectral diffusion increases as the

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molecule becomes more bent. Mechanical strain on the π system therefore promotes the molecule's sensitivity to environmental influences. Both blinking and spectral diffusion decrease under improved structural rigidity. Because fluorescence intermittency is a prerequisite to photobleaching,[34] we conclude that the extended chromophores are photochemically more stable.

The PL of MEH-PPV is strongly quenched and shifts to the blue upon photo-oxidation. This blue shift is generally attributed to a *reduction* in effective conjugation length due to oxidation.[6,7] Our data suggest an additional important effect: the bent polymer chromophores emit in the red and are less stable to environmental influences; consequently, they will oxidize first. With the lower energy units removed from the intramolecular energy transfer cascade,[1,6] excitation energy becomes trapped on the less-deformed units of higher energy, with the overall molecule thus emitting in the blue. Our preliminary calculations (Figure 1) indicate that the conjugation length (the oscillator strength) remains unchanged as the heptamers are bent and thus change their emission color. Concomitantly, we observe no wavelength dependence of the single-molecule emission intensity. Because these oligomers clearly serve as suitable models of polymer chromophores, we conclude that the emission wavelength of a polymer chromophore does not necessarily provide unambiguous information about its conjugation length. In contrast to general expectation, a spectral blue shift in MEH-PPV may therefore not be a direct signature of a change in actual π delocalization. This observation is important in view of the recent suggestion by Lee et al. that the observation of narrow transition lines in PPV in the blue spectral region of the ensemble emission may be a signature of oxidative effects.[35] Apparently, the opposite is true: the narrow transitions actually correspond to the most stable chromophores. However, emission from the blue narrow chromophores will only be observed if intramolecular excitation energy transfer can be switched off by working at sufficiently low temperatures.[36] Once thermally activated intramolecular excitation energy transfer occurs,[37] emission will arise from the lower energy broad emitting bent chromophores. In this context it is also rewarding to note that we recently succeeded in mapping the progression of narrow PL transition lines of a poly(*para*-phenylene) directly to the single-chain Raman scattering spectra,[38] demonstrating directly that it is indeed the narrowest transitions that correspond to the chemically purest species.

At present, our initial experiments cannot access all of the subtle details of the relation between chromophore bending and spectroscopy. Most importantly, bending need not relate directly to twisting of the chain, an important consideration to make when attempting to calculate the electronic structure.[18,23,24,39] For example, we take note that the Huang Rhys factor, given by the strength of the C=C vibronic progression, actually appears somewhat larger in the straight chromophore in Figure 2a than in the bent one, whereas the opposite is true for the polymer in Figure 2c. The Huang Rhys factor measures the strength of electron-phonon coupling, which is determined by the overall shift in molecular nuclear coordinates between the ground and excited state.[1] This shift arises from a change in bond alternation, which is in turn a measure of conjugation. We cannot presently make a conclusive statement about the effect of shape on conjugation length but can provide some indications. Bending of the chain in or out of the plane could potentially reduce intrachain twisting because it should enhance steric interactions between the side groups. This reduction in intrachain torsion could then actually improve conjugation, possibly explaining the red shift in emission of the more bent chromophores. The elongated chromophores would then be more twisted, experiencing greater excited-state relaxation and associated electron−phonon coupling. This assertion, however, appears in conflict with the observation of the linear Stark effect[28] in the elongated chromophores, which suggests that interring torsion is minimized to ensure all dipole inducing backbone substituents line up in a plane. In addition, we have previously reported that the strength of vibronic coupling in MEH-PPV can scatter widely from chromophore to chromophore.[26] Wavelength-dependent anisotropy measurements may provide further insight into the subtle interplay between ring torsion and chain bending. Although the lowest excited state probed in the present experiments is expected to give rise to a transition dipole oriented predominantly along the long molecular axis,[16] off-axis transitions have been identified at shorter wavelengths.[23] Further important questions include whether the relation between spectral broadening and bending can also be identified in single-chain PL excitation spectroscopy and whether time-resolved fluorescence can provide insight into the oscillator strength of transitions in dependence of chain bending, thereby providing important feedback to optimize quantum chemical models.

The *intramolecular* chain conformation of OPVs dramatically influences the photophysical properties. Because of the compelling spectroscopic similarities between oligomers and polymers, we propose that the key results apply to chromophores on the PPV chain. The observation of such a surprising variety of spectral signatures in isolated molecules should invite spectroscopists to revisit prior experiments on the assignment of aggregation phenomena.[20,21] We expect to be able to generalize at least some of the above observations to other polymer systems: although ladder-type polymers cannot bend and generally exhibit the same transition linewidth,[9,25] we have seen indications for a correlation between emission linewidth and chain bending in rigid β-phase polyfluorenes.[40] In the case of polyfluorene, however, such a correlation occurs only in the polarization anisotropy in *emission*, not in excitation. β-phase polyfluorene therefore indicates the presence of a spatially highly delocalized excitation rather than the strongly self-trapped exciton in the present case, which always gives rise to linearly polarized emission. A direct consequence of the present observations for device applications is that increasing the amount of elongated molecules could lead to a substantial increase in operating stability. Optimizing devices such as light-emitting diodes and solar cells in terms of stability and performance therefore requires direct control over the conformation of the individual chromophore by, for example, chemical encapsulation of the chain or bulk superstructure formation using block copolymers. We have thus far not been able to elucidate what actually drives the conformational variation of the conjugated chain in the matrix but only illuminate the role of shape in emission. Building on the experience of controlling the overall polymer chain (rather than the chromophore) conformation,[7,11] further investigations employing different matrices and preparation conditions are expected to reveal how certain preferential conformations can occur, which will in turn control the ensemble emission characteristics.

References and Notes

(1) Bässler, H.; Schweitzer, B. *Acc. Chem. Res.* **1999**, *32*, 173−182.

(2) Britton, G. *FASEB J.* **1995**, *9*, 1551−1558.

(3) Petek, H.; Bell, A. J.; Christensen, R. L.; Yoshihara, K. *J. Chem. Phys.* **1992**, *96*, 2412−2415.

(4) Knoll, K.; Krouse, S. A.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4424−4425.

(5) Schott, M. *J. Phys. Chem. B* **2006**, *110*, 15864−15868.

(6) Barbara, P. F.; Gesquiere, A. J.; Park, S. J.; Lee, Y. J. *Acc. Chem. Res.* **2005**, *38*, 602−610.

(7) Huser, T.; Yan, M.; Rothberg, L. J. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 11187−11191.

(8) Hu, D. H.; Yu, J.; Wong, K.; Bagchi, B.; Rossky, P. J.; Barbara, P. F. *Nature (London)* **2000**, *405*, 1030−1033.

(9) Schindler, F.; Lupton, J. M.; Feldmann, J.; Scherf, U. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 14695−14700.

(10) Feist, F. A.; Tommaseo, G.; Basché, T. *Phys. Rev. Lett.* **2007**, *98*, 208301.

(11) Sartori, S. S.; De Feyter, S.; Hofkens, J.; Van der Auweraer, M.; De Schryver, F.; Brunner, K.; Hofstraat, J. W. *Macromolecules* **2003**, *36*, 500−507.

(12) Hollars, C. W.; Lane, S. M.; Huser, T. *Chem. Phys. Lett.* **2003**, *370*, 393−398.

(13) White, J. D.; Hsu, J. H.; Fann, W. S.; Yang, S. C.; Pern, G. Y.; Chen, S. A. *Chem. Phys. Lett.* **2001**, *338*, 263−268.

(14) Forster, M.; Thomsson, D.; Hania, P. R.; Scheblykin, I. G. *Phys. Chem. Chem. Phys.* **2007**, *9*, 761−766.

(15) Müller, J. G.; Lupton, J. M.; Feldmann, J.; Lemmer, U.; Scherf, U. *Appl. Phys. Lett.* **2004**, *84*, 1183−1185.

(16) Hagler, T. W.; Pakbaz, K.; Heeger, A. J. *Phys. Rev. B* **1994**, *49*, 10968−10975.

(17) Baker, K. N.; Fratini, A. V.; Resch, T.; Knachel, H. C.; Adams, W. W.; Socci, E. P.; Farmer, B. L. *Polymer* **1993**, *34*, 1571−1587.

(18) Beenken, W. J. D.; Pullerits, T. *J. Phys. Chem. B* **2004**, *108*, 6164−6169.

(19) Ruseckas, A.; Wood, P.; Samuel, I. D. W.; Webster, G. R.; Mitchell, W. J.; Burn, P. L.; Sundström, V. *Phys. Rev. B* **2005**, *72*, 115214.

(20) Schwartz, B. J. *Annu. Rev. Phys. Chem.* **2003**, *54*, 141−172.

(21) Kim, J.; Swager, T. M. *Nature (London)* **2001**, *411*, 1030−1034.

(22) Fückel, B.; Hinze, G.; Diezemann, G.; Nolde, F.; Müllen, K.; Gauss, J.; Basché, T. *J. Chem. Phys.* **2006**, *125*, 144903.

(23) Chandross, M.; Mazumdar, S.; Liess, M.; Lane, P. A.; Vardeny, Z. V.; Hamaguchi, M.; Yoshino, K. *Phys. Rev. B* **1997**, *55*, 1486−1495.

(24) Tretiak, S.; Saxena, A.; Martin, R. L.; Bishop, A. R. *Phys. Rev. Lett.* **2002**, *89*, 097402.

(25) Schindler, F.; Jacob, J.; Grimsdale, A. C.; Scherf, U.; Müllen, K.; Lupton, J. M.; Feldmann, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 1520−1525.

(26) Schindler, F.; Lupton, J. M. *Chem. Phys. Chem.* **2005**, *6*, 926−937.

(27) Summers, M. A.; Kemper, P. R.; Bushnell, J. E.; Robinson, M. R.; Bazan, G. C.; Bowers, M. T.; Buratto, S. K. *J. Am. Chem. Soc.* **2003**, *125*, 5199−5203.

(28) Schindler, F.; Lupton, J. M.; Müller, J.; Feldmann, J.; Scherf, U. *Nat. Mater.* **2006**, *5*, 141−146.

(29) Scholes, G. D.; Larsen, D. S.; Fleming, G. R.; Rumbles, G.; Burn, P. L. *Phys. Rev. B* **2000**, *61*, 13670−13678.

(30) Kiraz, A.; Ehrl, M.; Bräuchle, C.; Zumbusch, A. *J. Chem. Phys.* **2003**, *118*, 10821−10824.

(31) Grell, M.; Bradley, D. D. C.; Ungar, G.; Hill, J.; Whitehead, K. S. *Macromolecules* **1999**, *32*, 5810−5817.

(32) Becker, K.; Lupton, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 7306−7307.

(33) Summers, M. A.; Bazan, G. C.; Buratto, S. K. *J. Am. Chem. Soc.* **2005**, *127*, 16202−16206.

(34) Hoogenboom, J. P.; van Dijk, E. M. H. P.; Hernando, J.; van Hulst, N. F.; García-Parajo, M. F. *Phys. Rev. Lett.* **2005**, *95*, 097401.

(35) Lee, Y. J.; Kim, D. Y.; Barbara, P. F. *J. Phys. Chem. B* **2006**, *110*, 9739−9742.

(36) Müller, J. G.; Lemmer, U.; Raschke, G.; Anni, M.; Scherf, U.; Lupton, J. M.; Feldmann, J. *Phys. Rev. Lett.* **2003**, *91*, 267403.

(37) Becker, K.; Lupton, J. M. *J. Am. Chem. Soc.* **2006**, *128*, 6468−6479.

(38) Walter, M.; Lupton, J. M.; Becker, K.; Feldmann, J.; Gaefken, G.; Höger, S. *Phys. Rev. Lett.* **2007**, *98*, 137401.

(39) Brédas, J. L.; Beljonne, D.; Coropceanu, V.; Cornil, J. *Chem. Rev.* **2004**, *104*, 4971−5003.

(40) Da Como, E.; Becker, K.; Feldmann, J.; Lupton, J. M. *Nano Lett.* **2007**, *7*, 2993−2998.