

Structure and Dynamics of Single Conjugated Polymer Chromophores by Surface-Enhanced Raman Spectroscopy

Zhenjia Wang and Lewis J. Rothberg*

Department of Chemistry, University of Rochester, Rochester, New York 14627

Fundamental interest in conjugated polymers derives from the quasi-one-dimensional properties bestowed on them by highly delocalized molecular orbitals.^{1,2} At the same time, these polymers are under investigation for applications to optoelectronic devices such as light-emitting diodes,³ solid-state lasers,⁴ and photovoltaics⁵ due to the combination of processability, conductivity, and visible optical gaps they afford. For these reasons, there is an extensive spectroscopic literature on conjugated polymers and oligomers.^{6–8} One of the recurrent themes in that body of work is the variability of conjugated polymer thin-film spectra with processing conditions^{9,10} that can be traced to the strong relationship between morphology and photophysics.^{8,11,12} In particular, interchain effects play an important role in both spectroscopy and photophysics. There remains some debate about the details of the interchain interactions, but one phenomenological picture that accounts for an enormous amount of the literature data is what is referred to as the “two-species model”, which posits that sample properties can be rationalized as linear combinations of two types of chromophores, those in “well-packed” regions of the sample where interchain processes are manifest and those that are “isolated” and solution-like.^{8,11,13}

The techniques of single-molecule spectroscopy were first applied to conjugated polymers by Barbara’s group^{14–16} with extraordinary results. The high molecular weight of the poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene (MEH-PPV) under study implied that it was composed of hundreds of individual chro-

ABSTRACT Dramatic localization of optical fields by interactions with surface plasmons on nanotextured metal surfaces allows us to record Raman spectra of individual chromophores on single chains of a high-molecular-weight model conjugated polymer, poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene. The data are broadly consistent with two configurations of the chromophore that are characteristic of packed and loose conformations of the backbone. Within these types, fluctuations of the chromophore planarity are observed, and we show how they can be analyzed by studying the temporal correlation of successive spectra. Chromophores exhibit some configurational memory on the time scale of minutes. We also observe substantial spectral fluctuations and associate these mostly with thermally induced motions of the chromophore in the “hot spot”. However, we also provide instances of data representing irreversible photochemistry as well as charging and discharging of the chromophore. Finally, we show that single chromophores embedded in the polymer reorganize in response to poor solvents.

KEYWORDS: nanotextured silver · conformational fluctuations · conjugated polymer vibrational spectroscopy · solvation

mophores, but single polymer chains exhibited behavior characteristic of single molecules, such as intensity blinking, correlation between incident and emission polarization, and sudden complete photobleaching. These data were interpreted to mean that efficient energy transfer to a single lowest energy chromophore dominated the spectroscopy and that the polymer was highly ordered into a “well-packed” structure. Huser and co-workers built upon this work to show that it was also possible to deposit individual MEH-PPV chains in extended geometries where they behaved as composites of many “isolated” chromophores and did not exhibit the characteristic behaviors enumerated above.¹⁷ More recent work on conjugated oligomers and polymers with finite numbers of active chromophores¹⁸ and on low-temperature spectroscopy of single chains^{19,20} continues to provide information and surprises about the nature of these systems.

*Address correspondence to rothberg@chem.rochester.edu.

Received for review September 6, 2007 and accepted October 18, 2007.

Published online November 30, 2007. 10.1021/nn700213t CCC: \$37.00

© 2007 American Chemical Society

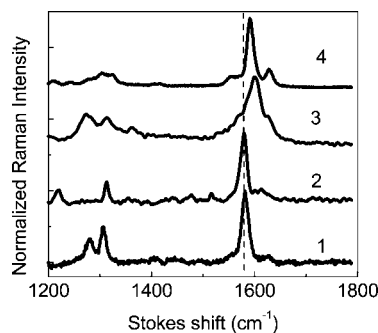


Figure 1. Normalized Raman spectra of MEH-PPV and an oligomeric analogue on nanotextured silver. Curve 1 is from a thin MEH-PPV film. Curves 2 and 3 are representative spectra of single MEH-PPV chains. Curve 4 presents the spectrum of a pentameric analogue of MEH-PPV.

Unfortunately, photoluminescence of large molecules in the condensed phase typically produces relatively diffuse spectra that provide limited structural information, even when studies can be performed at the single-molecule level, where the effects of inhomogeneity are presumably reduced. For this reason, it is desirable to pursue structurally sensitive techniques such as vibrational spectroscopy at the single-molecule level. Here, we report the first Raman spectra of single conjugated polymer chains at ambient temperatures and show that it is possible to obtain structural and dynamical information from such studies. Our work takes advantage of the pioneering work in single-molecule Raman spectroscopy by several groups,^{21–25} where it was proven that single molecules adsorbed in favorable locations (“hot spots”) on nanotextured silver and gold clusters or surfaces could be studied with Raman spectroscopy. The essential mechanism remains under study, but enhancement of local electromagnetic fields when light interacts with metal plasmons is an important component.^{26–28}

Raman spectra from single chains of high-molecular-weight MEH-PPV exhibit what we believe to be fascinating and unanticipated phenomenology. Surprisingly, we find that the vibrational spectra are also dominated by single chromophores. Moreover, the Raman spectra of single chains tend to be more complex than bulk MEH-PPV spectra, in contrast to the usual expectation that unraveling a bulk distribution leads to subsets of the full distribution. The spectra and intensities also fluctuate substantially with time, and we interpret this mostly in terms of thermally induced structural fluctuations. We introduce a spectral correlation analysis to show how the Raman spectroscopy can be applied to studying the motions that contribute to important configurational switches. In addition, we present examples of localized chromophore responses to photooxidation, exposure to solvents, and adventitious charging.

RESULTS AND DISCUSSION

Comparison of Single-Chain Raman Spectra with Bulk Spectra.

Figure 1 illustrates the “bulk” (~100 nm spin cast film)

TABLE 1. Prominent Raman Mode Frequencies and Assignments³⁰

assignment	MEH-PPV (bulk)	single MEH-PPV	single MEH-PPV	5PV	PPV (bulk)
vinyl C=C stretch	1620	1613	1628	1627	1625
ring C=C stretch	1582	1599	1581	1592	1582
ring C=C stretch	1556	1571	1554	1551	1546
vinyl C=C—H bend	1306	1309	1312	1318	1327
ring C=C—H bend	1280	1272	1265	1300	1301

spectra of MEH-PPV and the five-PV oligomeric analogue, along with two representative single-chain spectra. The bulk spectra are essentially the same with and without silver. Detailed mode assignments are presented elsewhere,²⁹ but here we focus on the high-frequency region, which is dominated by the backbone modes, as detailed in Table 1. The relative intensity of the ~1580 cm⁻¹ (ring stretch) and ~1620 cm⁻¹ (vinylene stretch) modes is a measure of conjugation length,^{30,31} with the latter nearly invisible when there is extended conjugation. This is evident from comparing the oligomer and polymer. As expected, the ring stretch is shifted to higher frequency due to stronger bond alternation in the oligomers.

Choosing instructive representative spectra is non-trivial and always prone to being somewhat subjective. Nevertheless, one simple classification of the chains that appears to be nearly universal includes the two types of characteristic spectra observed in the 155–1620 cm⁻¹ region of the spectrum, corresponding to the stretching of phenyl and vinyl groups on the backbones of MEH-PPV polymers. Roughly two-thirds of the spectral series we recorded were of the “diffuse” variety like those in trace 3 of Figure 1, while the remainder were of the “sharp” variety like those in trace 2. The latter tend to be highly conjugated, as measured by the relative intensity of ring and vinylenes stretches, suggesting intersegment interactions that reduce torsional flexibility. The former exhibit shorter conjugation, and the diffuse character suggests more inhomogeneity and flexibility. We think it is reasonable to associate these with the “isolated” and “well-packed” chromophores described in the introduction that appear to explain a wide variety of conjugated polymer phenomenology.

It is important to point out that any given chain exhibits only one of these types of spectra, even though all of the chains we studied exhibited interconversion between more and less highly conjugated states as well as considerable variation from spectrum to spectrum in other regions of the Raman spectrum. We will return to discuss the temporal fluctuations of the spectroscopy and dynamics of interconversion between more

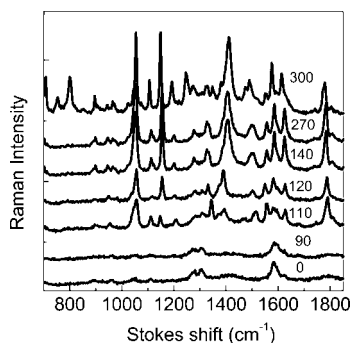


Figure 2. Selected spectra from a temporal series of Raman spectra of a single MEH-PPV chain under water. Integration times are 5 s.

and less highly conjugated geometries later in the paper. One other unexpected phenomenon that is evident in Figure 1 is something that we have found to be generally true of single-molecule Raman spectroscopy. In spite of our predisposition to think that single-molecule spectroscopy should select only part of an inhomogeneous distribution and therefore exhibit spectra sharper than the bulk spectrum, single-molecule Raman spectra are generally more complex and diffuse than the bulk spectra.³² We believe that this results from the texture of the field on the molecular length scale, caused by the plasmonic focusing of the light energy, and the interplay of that texture with molecular orientation.

Single-Chromophore Photochemistry. In discussing Figure 1, we presumed that we were looking at spectra from single chromophores in MEH-PPV chains, even though the chains have molecular weights of nearly 1 MD and would be expected to behave as molecular solids with many hundreds of chromophores (*i.e.*, independent conjugation segments). There is a variety of strong evidence that nearly all of the spectra we recorded represent only single chromophores that happen to register with hot spots on the substrate. First, we observe only isolated spots with Raman signal when we spatially scan our confocal microscope. These appear at densities similar to those for single-chain fluorescence spectroscopy^{14,17} and behave as would be expected with dilution of the sample from which the chains are spin cast. It is worth noting that the hot spots where we observe Raman scattering never appear to move, which suggests that the underlying silver morphology is stable. Second, we see sudden changes in spectroscopy that can be quite dramatic, including sudden and complete loss of Raman signal. One of the best examples of sudden spectroscopic changes is illustrated by the data of Figure 2, where we interpret the spectroscopy to show photooxidation of the polymer chromophore under study while recording Raman spectra under a drop of water. Assignment of the oxidized chromophore spectrum is straightforward and is consistent with the hypothesis that the photooxidation mechanism involves chain scission and terminal aldehyde

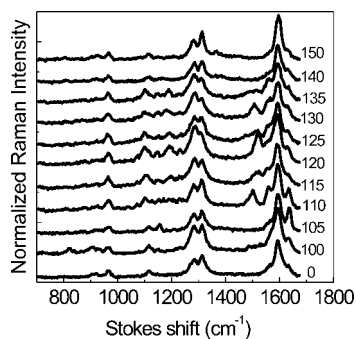


Figure 3. Selected spectra from a temporal series of Raman spectra from a MEH-PPV chain under air. The numbers represent the number of seconds after the initial spectrum. Integration times are 5 s.

formation.^{33,34} The carbonyl stretching mode at ~ 1800 cm^{-1} is clearly visible when the spectroscopy changes dramatically, and we have been able to repeat this result easily on a number of chains. After the carbonyl stretching mode appears, we see Raman spectra characteristic of benzene rings that do not participate in a more conjugated structure in the 1000 – 1600 cm^{-1} spectral window,²⁹ including the ring deformation at 1040 cm^{-1} . This is consistent with carbonyl groups in the oxidized MEH-PPV segments blocking the electronic delocalization.

It is interesting to consider why photooxidation not only fails to result in loss of Raman signal but generally increases the amount of Raman scattering. One might expect that chain scission and the attendant decrease in conjugation length would blue-shift the electronic resonance to be farther from that of the HeNe laser (632.8 nm) used as an excitation source. One might therefore expect a reduction in signal. We think that this unexpected behavior is strong evidence for the important role of charge-transfer resonance between molecules and silver as an enabler of single-molecule Raman scattering.^{21,25,26} In this particular case, it seems likely that the nonbonding state associated with the lone pair of the carbonyl group might transfer charge to the silver when photoexcited, to form a strong electronic resonance of the aldehyde–silver complex. This augments the electromagnetic enhancement by perhaps 2 or 3 orders of magnitude, to make single-molecule Raman scattering feasible.²⁶ Further study of the excitation spectrum of the Raman scattering may help to verify this hypothesis.

Polarons on Single Chromophores. Another clear signature of single-chromophore behavior in our studies is the relatively infrequent observation of charging and discharging of the chromophore under study. Assignment of spectra to cationic and anionic forms of the MEH-PPV backbone (“polarons”) is easily accomplished using the body of literature studying the Raman spectra of electrochemically doped conjugated polymers.^{35–37} The spectra in Figure 3 present an illustration of this behavior, where a strong mode at ~ 1500 cm^{-1} can be

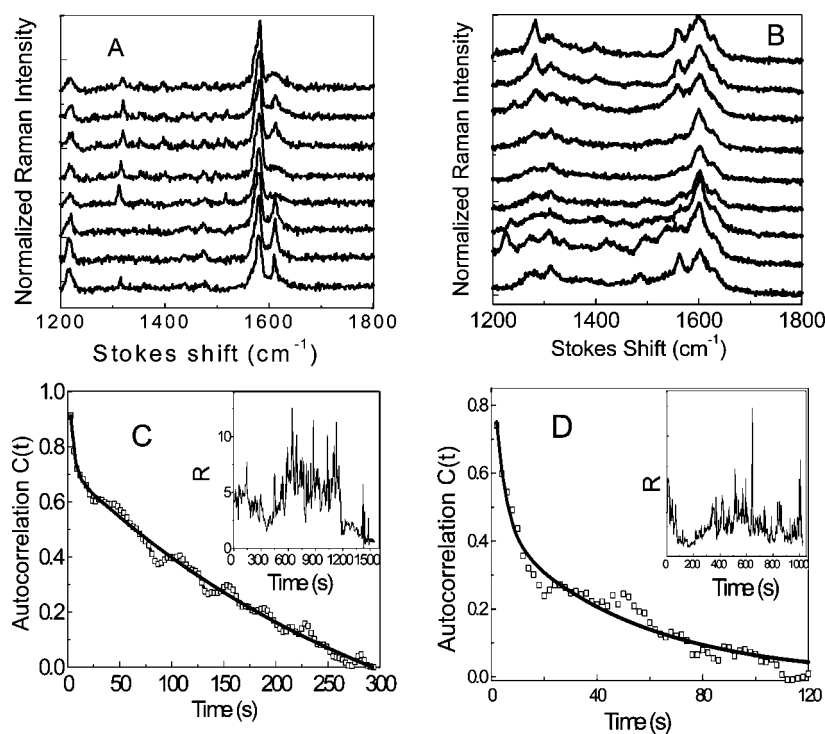


Figure 4. Raman spectra of two different chains of MEH-PPV and correlation analysis of their microscopic motions. Panels A and B are temporal series of spectra selected from chains where we are able to record hundreds of spectra apiece. Integration times are 3 s. The spectra of panels A and B are analyzed in panels C and D, respectively. The insets to panels C and D show the ratio R of the signal in the phenylene double-bond stretch ($\sim 1580\text{ cm}^{-1}$) versus that in the vinylene double-bond stretch ($\sim 1620\text{ cm}^{-1}$), which is a measure of chain planarity as discussed in the text. The autocorrelation values (\square) are plotted in the main portion of C and D, along with biexponential fits (—), as discussed in the text.

seen to appear and disappear along with other spectral features in the time window between 110 and 135 s. This mode is the red-shifted double-bond stretching mode as the conformation in the polaronic state becomes characteristically more quinoidal.

We note that the instances where we observe polarons are typically reversible and may suggest that we are not observing adventitious charging but rather photoexcitation of metastable polaron pairs, as is thought to occur in substantial quantum yield and is responsible for delayed luminescence.^{38–40} More work is needed to see whether the appearance of polaronic spectra is correlated with excitation intensity. In any event, the sudden appearance and disappearance of polaronic forms of the spectrum is also strong evidence that we are observing Raman scattering from only single chromophores.

Conformational Fluctuations of Single Chromophores. The ability to look at single chromophores provides us with a unique tool to separate the effects of static and dynamic disorder on conjugated polymer spectroscopy. Ensemble spectra cannot be used to differentiate between cases where each of the chromophores can assume many conformations some fraction of the time and cases where chromophore conformations are fixed but assume a distribution. Our data make it clear that

the vast majority of chromophores undergo substantial conformational fluctuations. Even absent the dramatic changes characteristic of charging and photochemistry portrayed above, there is significant time variation in the spectroscopy. More representative fluctuations are illustrated by the time series of spectra for two different single MEH-PPV chains shown in Figure 4A,B. The relative intensities of subsequent spectra also vary substantially, though this effect is artificially suppressed in the figure by normalization to the $\sim 1580\text{ cm}^{-1}$ mode intensity.

The variation in spectroscopy is most probably due to conformational dynamics. As noted previously, the ratio R of the $\text{C}=\text{C}$ double-bond stretching mode intensities for phenylene versus vinylene is a gauge of whether the chromophore is in its “isolated” or “well-packed” form. Thus, each of these chromophores seems to switch between short and long conjugation length, as would perhaps be caused by a ring twist in the chromophore backbone. The fluctuations are consistent with thermal motions of the molecules, and we found, as in previous work, that we could suppress them by putting a drop of liquid nitrogen on top of our sample.³² We also tried to enhance them by heating with a 488 nm beam from an

argon ion laser coincident on the spot with the 632.8 nm HeNe excitation laser. Remarkably, we saw no effect even when the argon laser was more intense than the HeNe. For the same reason that the HeNe is effectively focused by local plasmon resonance to a spot of a few nanometers around the chromophore under study, the 488 nm light energy is localized elsewhere and has little effect.

We can analyze the switching between these forms more quantitatively by computing the temporal autocorrelation of the time dependence of the ratio $R(t)$, $C(t) = \langle R(t)R(t+T) \rangle - \langle R(t) \rangle^2$, as essentially a measure of how long the chromophore “remembers” its degree of planarity. Figure 4C shows the autocorrelation of intensity ratios derived from the Figure 4A, while Figure 4D shows the analogous data for the autocorrelation computed from the data of Figure 4B. In each case, there is a fast ($\sim 3\text{ s}$) and a slow ($\sim 102\text{ s}$) component to the decay of the autocorrelation. The former is instrumentally limited and simply reflects the temporal spacing of the spectra as limited by signal integration time. Some loss of memory occurs, even on the time scale of several seconds. The slow decay component presumably reflects the time for a motion such as a hindered ring twist to occur in the local environment. Using an Arrhenius model with conformational flip rates of

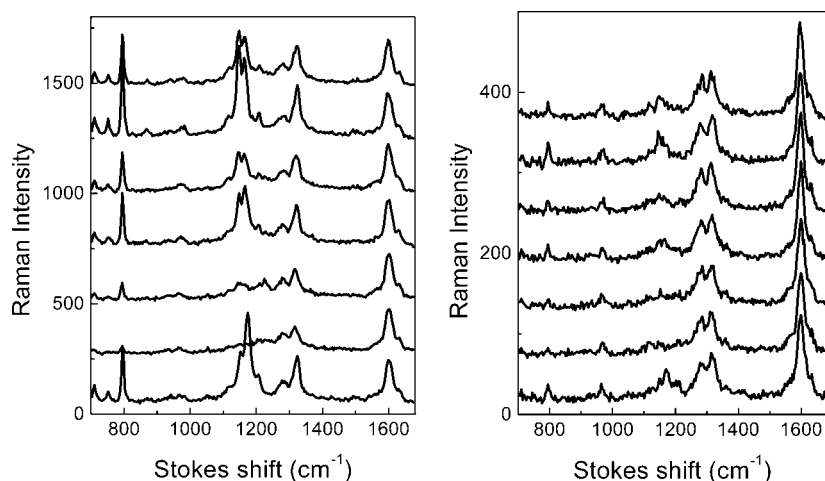


Figure 5. Corresponding selected spectra from two orthogonal polarizations of Raman scattering from a single chain of MEH-PPV. Time proceeds from bottom to top. Integration times are 5 s.

$10^{-2}/s$ and attempt frequencies of $10^{13}/s$, corresponding to torsional frequencies, gives a crude estimate of the associated barriers of 15 kcal/mol. This is nearly an order of magnitude higher than ring-flipping barriers computed *in vacuo*.⁴¹ The estimate based on our measurement may be larger because of steric hindrance from chain packing. To our knowledge, this is the first time that temporal correlation of single-chromophore Raman scattering has been used to analyze molecular dynamics, and we are in the process of increasing our statistical base so that more detailed conclusions can be reached. Performing temperature-dependent single-molecule Raman spectroscopy in conjunction with molecular dynamics simulations could provide substantial amounts of information on the microscopic origins of conformational changes in complex condensed-phase molecules.

Conformational Fluctuations of Side Groups. Another interesting phenomenon is that we sometimes observe distinct behavior in the Raman scattering from modes associated with the side groups. These are typically weak in the bulk Raman measurements but may experience substantial relative enhancement for certain fortuitous positions of the side groups in the electromagnetic hot spot. One example of spectra exhibiting this behavior is the temporal series of polarized Raman spectra shown in Figure 5. The modes at 1180 cm^{-1} (C–C–O antisymmetric stretch), 1320 cm^{-1} (methoxy twist/rock), and 800 cm^{-1} (C–C–O symmetric stretch) can be assigned to side-group motions. Evidence supporting that conjecture is provided by polarized spectroscopy, where spectra with orthogonal scattered polarization are recorded simultaneously. Figure 6 plots the ratio of mode intensities for a series of spectra associated with the chromophore in Figure 5, which shows that some of the modes tend to be represented more strongly in different polarizations and, moreover, that

some have stable relative intensities between polarizations while others fluctuate.

Unfortunately, we do not know the near-field polarization of the excitation source relative to the molecular orientation in the hot spot. Undoubtedly, one of the consequences of the plasmonic focusing is to make the polarization elliptical, containing even components in the propagation direction of the light, making it highly dependent on the detailed geometry of the individual hot spot. The polarization may even be quite nonuniform

within a given hot spot. In fact, we cannot even conceive in principle of how the near-field polarization could be determined experimentally. Nevertheless, we can say that hot spot characteristics appear to be constant with time so that, once again, fluctuations in the relative amounts of signal in orthogonal scattered polarizations reflect molecular motion. In the case of the molecule in Figure 6, only some of the modes change relative intensity with time. In particular, the four modes with filled-in circles ($1148, 795, 1166, \text{ and } 1324\text{ cm}^{-1}$) exhibit obvious changes in ratio in spectra numbers 10, 13, 16, and 17, while the others do not. Remarkably, each of the modes that exhibits ratio changes is associated with the side groups. This both tends to confirm our assignments above and illustrates that the Raman variations reflect molecular motion within the hot spot.

Solvent Effects on Single-Chromophore Geometry. One area of study in polymer science that has been extremely productive concerns how polymers respond conformationally to changes in solvent.^{42–44} The Raman measurement provides us with the ability to ask similar sorts of questions at the single-chromophore level. On the

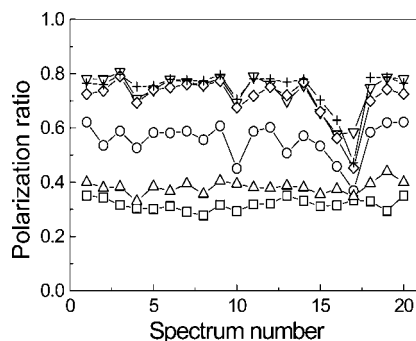


Figure 6. Ratio of Raman intensity in two orthogonal polarizations in a sequence of spectra of the single chain of MEH-PPV studied in Figure 5. The spectra are spaced by 5 s each and have 5 s integration times.

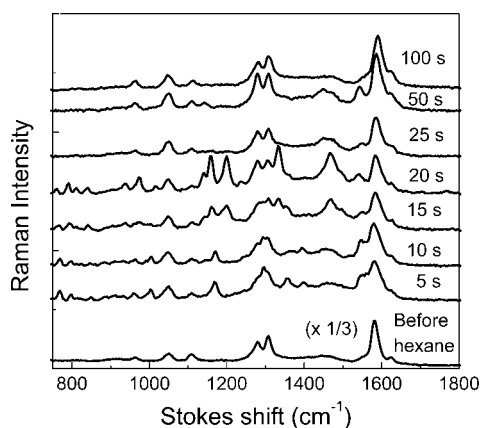


Figure 7. Solvent effect on the conformational changes of a chromophore on a single MEH-PPV chain. Selected spectra before and after immersion of the chain under a drop of hexane. Integration times are 5 s, and the labeled times are the number of seconds after application of the hexane.

basis of the results above, where side-group motions could be observed when the polymer backbone was apparently unaffected, we reasoned that it would be interesting to look at what happens to the geometry of a chromophore when exposed to a solvent that is generally considered to be poor (so that it does not dissolve the polymer) but would be considered to be a “good solvent for the side groups”. Figure 7 presents data for a single chain of MEH-PPV before addition of a drop of hexane on top and tracks the behavior for several minutes after addition of hexane until the hexane evaporates. Indeed, the 1180 cm^{-1} mode characteristic of the side groups appears in the spectra between 5 and 20 s and disappears when the hexane evaporates. At the same time, the chain seems to be twisted in hexane to form a less conjugated structure with a corresponding red shift in the phenylene double-bond modes.

CONCLUSIONS AND FUTURE WORK

Using confocal microscopy, we are able to observe Raman scattering from isolated conjugated polymer chains on a nanotextured silver surface. We routinely

observe the vibrational spectrum of single chromophores (conjugation segments) in the polymer in spite of the fact that the chain must have hundreds of chromophores. To our knowledge, this is the first such observation at 300 K, and it provides a remarkable demonstration of optical field localization to the $<5\text{ nm}$ scale by interactions with surface plasmons. The chromophores divide roughly into those with broad spectra and those with narrower spectra, and we associate these with loose and packed geometries, respectively. We observe fluctuations of the conjugation length in each of these packing conformations, though more so in the loose ones, and some structural memory on the time scale of a few minutes. There are considerable fluctuations in the spectra, and we ascribe most of these to motions of the chromophore under study with respect to the highly textured optical field pattern in the Raman-active “hot spot”. Nevertheless, we also observe some spectral changes that we associate with photooxidation and with charging of the chromophore under study.

The research we have presented here raises many intriguing possibilities but also leaves many daunting questions. It provides an initial glimpse into the unusual phenomenology of single-chromophore Raman scattering, but a huge amount of work will be needed to obtain a deeper and more microscopic understanding. We think that the use of temporal correlation is an excellent window into the relevant molecular dynamics and hope that it will evolve into a widely used analytical tool. Temperature-dependent studies would be of particular importance in sorting out the relevant motions and barriers to conformational switching, and we plan these in the near future. Similarly, our data make it clear that a great deal could be learned by combining systematic doping and solvent studies with single-chain Raman spectroscopy. We hope that this will stimulate creative work to understand and exploit these fascinating phenomena.

METHODS

Nanotextured silver films were fabricated on glass coverslips using the Tollens reaction⁴⁵ according to the prescription of ref 46. Precipitation of silver nanoparticles and clusters for predetermined optimized exposure times makes excellent substrates that support single-molecule Raman scattering over a large range of frequencies.⁴⁷ The synthesis and characterization of the MEH-PPV have been described previously.⁴⁸ MEH-PPV chains were spin-cast onto these silver substrates from toluene solutions with a concentration of 10^{-4} mg/mL , similar to the concentrations used in single-molecule fluorescence studies of conjugated polymers. We also spin-cast at high concentration of MEH-PPV to form thin films on substrates with and without silver coatings for comparison to single chains. Excitation and collection of Raman scattering were measured in a scanning confocal microscope with a 1.4 numerical aperture oil-immersion objective. The excitation source was a HeNe laser operating at 632.8 nm . After removal of scattering of the excitation light with

a holographic notch filter, the remaining light was observed using either a spectrometer with a liquid-nitrogen-cooled charge-coupled device (CCD) detector to measure spectra or a single-photon-counting photomultiplier with a $100\text{ }\mu\text{m}$ pinhole to image samples and to measure total Raman scattering intensity versus time. Raman images were acquired by scanning the sample with a computer-controlled 2D piezoelectrically driven scanning stage. Spectroscopy and dynamics of molecules were studied at “hot spots” exhibiting high Raman intensity that are located using the spatial scans. We were also able to simultaneously measure orthogonally polarized components of the Raman spectra by utilizing a beam-displacing Wollaston prism at the spectrometer input so that different polarizations imaged in different strips on the CCD camera.

Acknowledgment. We are grateful to NSF grants DMR-0309444 and DMR-0513416 for support. We also thank Dr. Mary

Galvin for supplying oligomeric phenylenevinylens and Dr. Paul Barbara for his encouragement of this work.

REFERENCES AND NOTES

- Barbara, P. F.; Gesquire, A. J.; Park, S. J.; Lee, Y. J. Single-Molecule Spectroscopy of Conjugated Polymers. *Acc. Chem. Res.* **2005**, *38*, 602–610.
- Winokur, M. J.; Chunwachirasiri, W. Nanoscale Structure-Property Relationships in Conjugated Polymers: Implications for Present and Future Device Applications. *J. Polym. Sci. B* **2003**, *41*, 2630–2648.
- Friend, R. H. Conjugated Polymers. New Materials for Optoelectronic Devices. *Pure Appl. Chem.* **2001**, *73*, 425–430.
- McGehee, M. D.; Heeger, A. J. Semiconducting (Conjugated) Polymers as Materials for Solid-State Lasers. *Adv. Mater.* **2000**, *12*, 1655–1668.
- Hoppe, H.; Sariciftci, N. S. Organic Solar Cells: An Overview. *J. Mater. Res.* **2004**, *19*, 1924–1945.
- Cornil, J.; Beljonne, D.; Heller, C. M.; Campbell, I. H.; Layrich, B. K.; Smith, D. L.; Bradley, D. D. C.; Mullen, K.; Bredas, J. L. Photoluminescence Spectra of Oligo-Paraphenylenevinylens: a Joint Theoretical and Experimental Characterization. *Chem. Phys. Lett.* **1997**, *278*, 139–145.
- Jiang, X. M.; Osterbacka, R.; Korovyanko, O.; An, C. P.; Horovitz, B.; Janssen, R. A. J.; Vardeny, Z. V. Spectroscopic Studies of Photoexcitations in Regioregular and Regiorandom Polythiophene Films. *Adv. Funct. Mater.* **2002**, *12*, 587–597.
- Rothberg, L. J. Photophysics of Conjugated Polymers. In *Semiconducting Polymers: Chemistry, Physics and Engineering*; Hadziannou, G., and Malliaras, G., Eds.; Wiley-VCH Verlag GmbH: Weinheim, 2006; pp 179–204.
- Schwartz, B. J. Conjugated Polymers as Molecular Materials: How Chain Conformation and Film Morphology Influence Energy Transfer and Interchain Interactions. *Annu. Rev. Phys. Chem.* **2003**, *54*, 141–172.
- Peng, K. Y.; Chen, S. A.; Fann, W. S.; Chen, S. H.; Su, A. C. Well-Packed Chains and Aggregates in the Emission Mechanism of Conjugated Polymers. *J. Phys. Chem. B* **2005**, *109*, 9368–9373.
- Collison, C. J.; Rothberg, L. J.; Tremaneeekarn, V.; Li, Y. Conformational Effects on the Photophysics of Conjugated Polymers: A Two Species Model for MEH-PPV Spectroscopy and Dynamics. *Macromolecules* **2001**, *34*, 2346–2352.
- Spano, F. C. Modeling Disorder in Polymer Aggregates: The Optical Spectroscopy of Regioregular Poly(3-hexylthiophene) Thin Films. *J. Chem. Phys.* **2005**, *122*, 234701.
- Jakubiak, R.; Bao, Z.; Rothberg, L. J. Dendritic Sidegroups as Three-Dimensional Barriers to Aggregation Quenching of Conjugated Polymer Fluorescence. *Synth. Met.* **2000**, *114*, 61–64.
- Yu, J.; Hu, D.; Barbara, P. F. Unmasking Electronic Energy Transfer of Conjugated Polymers by Suppression of O-2 Quenching. *Science* **2000**, *289*, 1327.
- Hu, D.; Yu, J.; Wong, K.; Bagchi, B.; Rossky, P. J.; Barbara, P. F. Collapse of Stiff Conjugated Polymers with Chemical Defects into Ordered, Cylindrical Conformations. *Nature* **2000**, *405*, 1030–1033.
- Lee, Y. J.; Kim, D. Y.; Barbara, P. F. Single Conjugated Polymer Spectroscopy: Effect of Sample Preparation and Excitation Conditions. *J. Phys. Chem. B* **2006**, *110*, 9739–9742.
- Huser, T.; Yan, M.; Rothberg, L. J. Single Chain Spectroscopy of Conformational Dependence of Conjugated Polymer Photophysics. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 11187–11191.
- White, J. D.; Hsu, J. H.; Yang, S. C.; Fann, W. S.; Pern, G. Y.; Chen, S. A. Deduction of the Conformation of Short Chain Luminescent Conjugated Polymers from Single Molecule Photophysics. *Chem. Phys. Lett.* **2001**, *338*, 263–268.
- Schindler, F.; Lupton, J. M. Single Chromophore Spectroscopy of MEH-PPV: Homing-in on the Elementary Emissive Species in Conjugated Polymers. *Chem. Phys. Chem.* **2005**, *6*, 926–934.
- Walker, M. J.; Lupton, J. M.; Becker, K.; Feldmann, J.; Gaefke, G.; Hoger, S. Simultaneous Raman and Fluorescence Spectroscopy of Single Conjugated Polymer Chains. *Phys. Rev. Lett.* **2007**, *98*, 137401.
- Nie, S.; Emery, S. R. Probing Single Molecules and Single Nanoparticles by Surface-Enhanced Raman Scattering. *Science* **1997**, *275*, 1102–1106.
- Kneipp, K.; Wang, Y.; Kneipp, H.; Perelman, L. T.; Itzkan, I.; Dasari, R.; Feld, M. S. Single Molecule Detection Using Surface-Enhanced Raman Scattering (SERS). *Phys. Rev. Lett.* **1997**, *78*, 1667–1670.
- Kneipp, K.; Kneipp, H. Surface-Enhanced Raman Scattering on Silver Nanoparticles in Different Aggregation Stages. *Isr. J. Chem.* **2006**, *46*, 299–305.
- Xu, H.; Bjerneld, E. J.; Kall, M.; Borjesson, L. Spectroscopy of Single Hemoglobin Molecules by Surface Enhanced Raman Scattering. *Phys. Rev. Lett.* **1999**, *83*, 4357–4360.
- Michaels, A. M.; Jiang, J.; Brus, L. Ag Nanocrystal Junctions as the Site for Surface-enhanced Raman Scattering of Single Rhodamine 6G Molecules. *J. Phys. Chem. B* **2000**, *104*, 11965–11971.
- Moskovits, M. Surface-Enhanced Spectroscopy. *Rev. Mod. Phys.* **1985**, *57*, 783–826.
- Li, K.; Stockman, M. I.; Bergman, D. J. Self-Similar Chain of Metal Nanospheres as an Efficient Nanolens. *Phys. Rev. Lett.* **2003**, *91*, 227402.
- Sarychev, A. K.; Shalaev, V. M. Theory of Nonlinear Optical Responses in Metal-Dielectric Composites. *Top. Appl. Phys.* **2002**, *82*, 169–184.
- Dollish, F. R.; Fateley, W. G.; Bentley, F. F. *Characteristic Raman Frequencies of Organic Compounds*; John Wiley & Sons, Inc.: New York, 1974.
- Baitoul, M.; Wery, J.; Buisson, J. P.; Arbucl, G.; Shah, H.; Lefrant, S.; Hamdoume, M. In Situ Resonant Raman and Optical Investigations of p-Doped Poly (p-phenylene vinylene). *Polymer* **2000**, *41*, 6955–6954.
- Sakamoto, A.; Furukawa, Y.; Tasumi, M. Infrared and Raman Studies of Poly(p-phenylenevinylene) and its Model Compounds. *J. Phys. Chem.* **1992**, *96*, 1490–1494.
- Wang, Z.; Rothberg, L. J. Origins of Blinking in Single-Molecule Raman Spectroscopy. *J. Phys. Chem. B* **2005**, *109*, 3387–3391.
- Yan, M.; Rothberg, L. J.; Papadimitrakopoulos, F.; Galvin, M. E.; Miller, T. M. Defect Quenching of Conjugated Polymer Luminescence. *Phys. Rev. Lett.* **1994**, *73*, 744–747.
- Papadimitrakopoulos, F.; Yan, M.; Rothberg, L. J.; Katz, H. E.; Galvin, M. E. Thermal and Photochemical Origin of Carbonyl Group Defects in Poly-(p-phenylenevinylene). *Mol. Cryst. Liq. Cryst.* **1994**, *256*, 663–669.
- Tian, B.; Zerbi, G.; Mullen, K. Electronic and Structural Properties of Polyparaphenylenevinylene from the Vibrational Spectra. *J. Chem. Phys.* **1991**, *95*, 3198–3207.
- Sakamoto, A.; Furukawa, Y.; Tasumi, M. Resonance Raman Characterization of Polarons and Bipolarons in Sodium-Doped Poly(para-phenylenevinylene). *J. Phys. Chem.* **1992**, *96*, 3870–3874.
- Orion, I.; Buisson, J. P.; Lefrant, S. Spectroscopic Studies of Polaronic and Bipolaronic Species in n-Doped Poly(paraphenylenevinylene). *Phys. Rev. B* **1998**, *57*, 7050–7065.
- Gerhard, A.; Bässler, H. Delayed Fluorescence of a Poly (p-phenylenevinylene) Derivative: Triplet-Triplet Annihilation Versus Geminate Pair Recombination. *J. Chem. Phys.* **2002**, *117*, 7350–7356.
- Rothberg, L. J.; Yan, M.; Papadimitrakopoulos, F.; Galvin, M. E.; Kwock, E. W.; Miller, T. M. Photophysics of Phenylenevinylene Polymers. *Synth. Met.* **1996**, *80*, 41–58.
- Cuppoletti, C. M.; Rothberg, L. J. Persistent Photoluminescence in Conjugated Polymers. *Synth. Met.* **2003**, *139*, 867–871.

41. Pan, J. F.; Chua, S. J.; Huang, W. Conformational Analysis of Trimethylsilyl Substituted Trans-Stilbenes: Modeling of Torsions in Silicon-Containing Poly(p-phenylenevinylene). *Chem. Phys. Lett.* **1999**, *315*, 233–238.
42. Schaller, R. D.; Lee, L. F.; Johnson, J. C.; Haber, L. H.; Saykally, R. J.; Vieceli, J.; Benjamin, I.; Nguyen, T. Q.; Schwartz, B. J. The Nature of Interchain Excitations in Conjugated Polymers: Spatially-Varying Interfacial Solvatochromism of Annealed MEH-PPV Films Studied by Near-Field Scanning Optical Microscopy (NSOM). *J. Phys. Chem. B* **2002**, *106*, 9496–9506.
43. Hsu, J. H.; Fann, W. S.; Tsao, P. H.; Chuang, K. R.; Chen, S. A. Fluorescence from Conjugated Polymer Aggregates in Dilute Poor Solution. *J. Phys. Chem. A* **1999**, *103*, 2375–2380.
44. Nguyen, T. Q.; Doan, V.; Schwartz, B. J. Conjugated Polymer Aggregates in Solution: Control of Interchain Interactions. *J. Chem. Phys.* **1999**, *110*, 4068–4078.
45. Saito, Y.; Wang, J. J.; Smith, D. A.; Batchelder, D. N. A Simple Chemical Method for the Preparation of Silver Surfaces for Efficient SERS. *Langmuir* **2002**, *18*, 2959–2961.
46. Wang, Z.; Pan, S.; Krauss, T. D.; Du, H.; Rothberg, L. J. The Structural Basis for Giant Enhancement Enabling Single-Molecule Raman Scattering. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 8638–8643.
47. Wang, Z.; Rothberg, L. J. Silver Nanoparticle Coverage Dependence of Surface-Enhanced Raman Scattering. *Appl. Phys. B: Laser Opt.* **2006**, *84*, 289–293.
48. Hsieh, B. R.; Yu, Y.; Vanlaeken, A. C.; Lee, H. General Methodology Toward Soluble Poly(p-phenylenevinylene) Derivatives. *Macromolecules* **1997**, *30*, 8094–8095.