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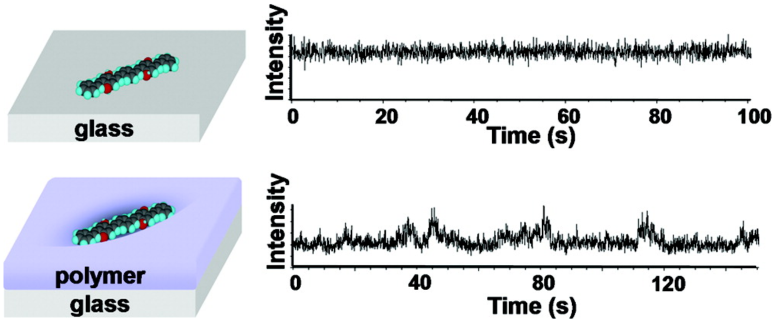

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Matrix-Induced Intensity Fluctuations in the Fluorescence from Single Oligo(phenylenevinylene) Molecules

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Abstract: Single molecule spectroscopy on oligo(phenylenevinylene) (OPV) chromophores shows that the fluorescence intermittency strongly correlates to the rigidity of the environment surrounding the molecules. For OPV single molecules, environmental rigidity inhibits twisting about the vinyl linkages, the molecular motion associated with the observed "off" (nonabsorbing) state. By increasing the rigidity of a single molecule's environment, we can tune its room temperature fluorescence from rapid, sub-millisecond "blinking" fluctuations (fluid polymer environment) to completely "on" with no blinking observed (molecules adsorbed to a rigid bare glass substrate). The difference in fluorescence intermittency from environment to environment is immediately apparent and explicit in single molecule intensity trajectories under cw (continuous wave) excitation, demonstrating the sensitivity of these chromophores to their surroundings and emphasizing the importance of morphological control in real-world applications involving phenylenevinylene-based materials.

Introduction

In thin films used in molecular electronics such as polymer organic light-emitting diodes (OLEDs) or polymer photovoltaic cells, the amorphous nature of polymeric materials means that individual chromophores will exist in a range of nanoscale environments. Single molecule (SM) experiments on conjugated polymer and oligomer molecules in nonluminescent amorphous polymer films can help predict the effect of bulk film characteristics on the photophysics of individual molecules and chromophores within these devices. It is now well established that film morphology is a critical parameter in the electrooptic properties of conjugated polymer films.[1] To understand the fundamental interplay between structure and property in these materials, it is important to understand how the macroscopic film morphology influences the nanoscale environment surrounding individual chromophores.

Single fluorescent molecules are sensitive probes of their surroundings.[2,3] Data extracted from SM experiments including fluorescence intensity trajectories, spectral shape and position, and fluorescence lifetimes can be used to investigate the chemical and physical characteristics of the surrounding medium. For example, recent work has demonstrated that the charge-transfer spectra of single dye molecules are very sensitive to the polarizability of their surroundings and enable nanoscale characterization of thin polymer films.[4−7] Recent experimental and theoretical reports have demonstrated how a fluctuating dielectric nanoenvironment surrounding a polarizable probe molecule gives rise to a distribution of measured fluorescence lifetimes.[8,9] Single molecule experiments can also help to predict how the physical environment surrounding molecules will affect their emissive properties. Single molecules embedded in polymer matrixes near their glass-transition temperature have been used to characterize the physics of polymers undergoing phase transitions.[10,11] Single molecule photophysics reveal that the conformations adopted by isolated conjugated polymers in polystyrene matrixes vary according to the average molecular weight of the polystyrene used.[12] Flexible dye molecules are sensitive to the rigidity and polarity of their surroundings.[13,14] Energy transfer between single donor−acceptor pairs bound by flexible molecules such as DNA or proteins can be used to monitor the effects of external factors on molecular conformation.[15,16] In all of these studies, the fluorescent probe molecule is used as a probe of its surroundings. For compounds used in organic devices, however, we wish to use the surroundings to

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(1) Schwartz, B. J. *Annu. Rev. Phys. Chem.* **2003**, *54*, 141−172.
(2) Macklin, J. J.; Trautman, J. K.; Harris, T. D.; Brus, L. E. *Science* **1996**, *272*, 255−258.
(3) Kumbhakar, M.; Nath, S.; Mukherjee, T.; Mittal, J. P.; Pal, H. *J. Photochem. Photobiol., C: Photochem. Rev.* **2004**, *5*, 113−137.
(4) Hou, Y. W.; Higgins, D. A. *J. Phys. Chem. B* **2002**, *106*, 10306−10315.
(5) Bardo, A. M.; Collinson, M. M.; Higgins, D. A. *Chem. Mater.* **2001**, *13*, 2713−2721.
(6) Bardo, A. M.; Collinson, M. M.; Higgins, D. A. *Chem. Mater.* **2001**, *13*, 3058−3058.
(7) Hou, Y. W.; Bardo, A. M.; Martinez, C.; Higgins, D. A. *J. Phys. Chem. B* **2000**, *104*, 212−219.
(8) Vallee, R. A. L.; Tomczak, N.; Kuipers, L.; Vancso, G. J.; van Hulst, N. F. *Chem. Phys. Lett.* **2004**, *384*, 5−8.
(9) Vallee, R. A. L.; Van Der Auweraer, M.; De Schryver, F. C.; Beljonne, D.; Orrit, M. *Chemphyschem* **2005**, *6*, 81−91.
(10) Deschenes, L. A.; Vanden Bout, D. A. *Science* **2001**, *292*, 255−258.
(11) Biju, V. P.; Ye, J. Y.; Ishikawa, M. *J. Phys. Chem. B* **2003**, *107*, 10729−10735.
(12) 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.
(13) Willets, K. A.; Callis, P. R.; Moerner, W. E. *J. Phys. Chem. B* **2004**, *108*, 10465−10473.
(14) Yu, J.; Hu, D. H.; Barbara, P. F. *Science* **2000**, *289*, 1327−1330.
(15) Yang, H.; Xie, X. S. *J. Chem. Phys.* **2002**, *117*, 10965−10979.
(16) Ha, T.; Enderle, T.; Ogletree, D. F.; Chemla, D. S.; Selvin, P. R.; Weiss, S. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 6264−6268.

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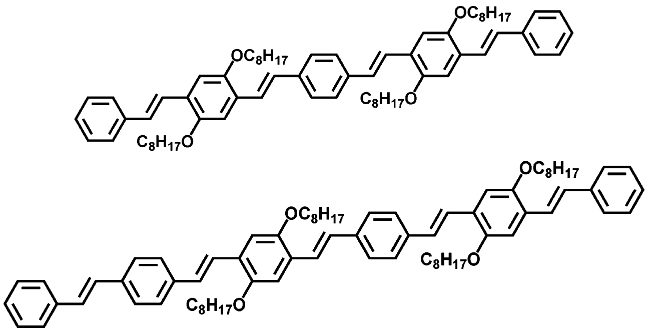
Chart 1. The Oligo(phenylenevinylene) Molecules (5OPV and 6OPV) Used in This Study



probe the photophysics of the chromophore itself to explore the effects of film morphology on individual chromophores.

Oligo(phenylenevinylene) molecules with five and six phenyl rings along the oligomer backbone are single chromophore analogues of longer chain phenylenevinylene-based polymers (Chart 1).[17] In a previous article, we explored the role of cis defects on the photophysical properties of these single oligo(phenylenevinylene) molecules.[18] In this article, we turn our attention to the role that the external environment plays in a SM's photophysics, with particular emphasis on conformational freedom. We have shown that freedom of motion is an important factor in the single molecule photophysics of the tetrahedral oligo(phenylenevinylene).[19] In this article, we extend the study of conformational freedom of single OPV molecules to include the influence of external factors, and we relate these findings to the molecular structure of OPV molecules.

Perhaps the simplest oligo(phenylenevinylene) molecule, stilbene is a two phenyl analogue of an OPV and is a molecule that has generated a large body of research over the years.[20−23] Pioneering studies showed that the fluorescence quantum yields of both *cis*- and *trans*-stilbene increase with increasing solvent viscosity.[22,23] As the viscosity of the surrounding media increases, nonradiative molecular motion becomes energetically costly, and the radiative pathway to the ground state becomes favorable. Bending and twisting motions about the central double bond are the molecular motions linked to nonradiative pathways. When twisting is prohibited by a viscous solvent,[23] low temperature,[24] or increased structural rigidity of the molecule,[21] the fluorescence quantum yield of *cis*- and *trans*-stilbene and nonplanar *trans*-stilbene derivatives becomes increasingly higher. Solvent viscosity has also been shown to enhance the fluorescence quantum yield of longer chain OPV molecules similar to our 5OPV and 6OPV.[25] Solvent polarity does not in general have as significant an effect on the fluorescence yield of the stilbenes.[23]

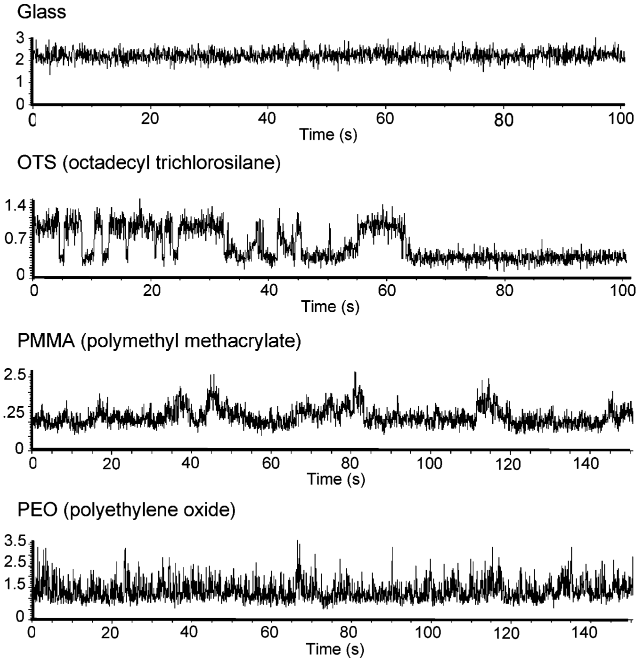
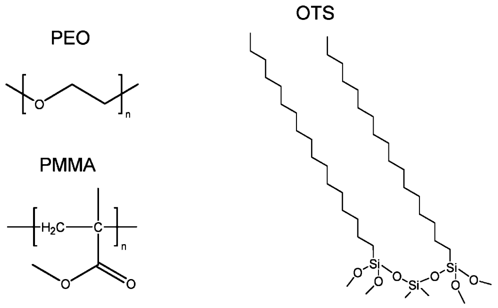


Figure 1. Intensity trajectories of 5OPV molecules adsorbed the four different substrates used in this study. The intensity trajectories shown here are representative examples of $>$75 single molecules probed on each surface (128 ms bin time).

Chart 2. Chemical Structures of Surface Modifiers



The chemical structures of the surface-modifying molecules are found in Chart 2. Details about surface and sample preparation may be found in the Supporting Information for this article, and our single molecule spectroscopy apparatus has been described in previous studies.[17,18,25] Poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) are spin cast as thin films; octadecyltrioxysilane (OTS) monolayers are chemically deposited onto glass surfaces.

Results

Intensity Trajectories. Figure 1 shows representative intensity trajectories for single 5OPV molecules prepared in each of the four environments investigated. The intensity trajectories were collected using roughly the same excitation power. The trajectories illustrate the overall trend observed from intensity trajectories recorded from at least 75 single molecules in each environment. The differences in intensity fluctuations are striking and unprecedented in single molecule literature. By changing the nature of the surface the molecule is adsorbed to, we can tune the SM blinking behavior from continuously "on"

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(17) Wang, S. J.; Oldham, W. J.; Hudack, R. A.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 5695−5709.

(18) 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.

(19) Summers, M. A.; Robinson, M. R.; Bazan, G. C.; Buratto, S. K. *Chem. Phys. Lett.* **2002**, *364*, 542−549.

(20) Schultefrohlinde, D.; Blume, H.; Gusten, H. *J. Phys. Chem.* **1962**, *66*, 2486−2491.

(21) Saltiel, J.; Zafrion, O. C.; Megarity, E. D.; Lamola, A. A. *J. Am. Chem. Soc.* **1968**, *90*, 4759.

(22) Gegiou, D.; Muszkat, K. A.; Fischer, E. *J. Am. Chem. Soc.* **1968**, *90*, 3907−3918.

(23) Sharafy, S.; Muszkat, K. A. *J. Am. Chem. Soc.* **1971**, *93*, 4120−4125.

(24) Gegiou, D.; Muszkat, K. A.; Fischer, E. *J. Am. Chem. Soc.* **1968**, *90*, 0, 3907−3918.

(25) Oelkrug, D.; Tompert, A.; Gierschner, J.; Egelhaaf, H. J.; Hanack, M.; Hohloch, M.; Steinhuber, E. *J. Phys. Chem. B* **1998**, *102*, 1902−1907.

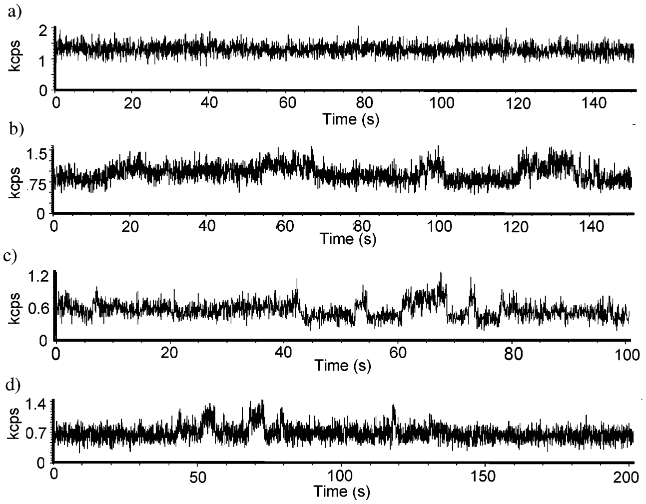

Figure 2. Intensity trajectories for four different single molecules adsorbed to OTS surfaces demonstrating the range of dynamics observed for molecules in this environment.

(5OPV on glass) to mostly "off" (5OPV on/in a PEO film). We observe similar intensity trajectories with the same trend in fluorescence dynamics for single 6OPV molecules. As we have previously noted, OPV molecules adsorbed to bare glass surfaces do not exhibit ms on/off blinking behavior.[18]

The largest variation in dynamics is found for molecules adsorbed to OTS (Figure 2), where some molecules blinked very little or not at all (Figure 2a), other molecules exhibited more rapid "flickering" intensity trajectories (Figure 2b), and most molecules exhibited on and off blinking on the millisecond to second time scale (Figure 2c and 2d). The different blinking dynamics observed for the OTS substrate oligomers most likely arise from the different environments present on this sample. AFM images of the OTS substrates reveal islands of close-packed OTS surrounded by areas of bare or sparsely coated glass. The molecules that exhibit static intensity trajectories (Figure 2a) may be adsorbed to bare glass regions between OTS islands.

The SM intensity trajectories obtained from molecules in a PEO environment are characterized by rapid, short bursts of emission on a millisecond time scale. Each intensity trajectory obtained from this substrate closely resembles the trajectory shown in Figure 1d. The peak-to-baseline ratio of these "grassy" intensity trajectories is significantly larger than the signal-to-noise of the instrument at the laser powers used.

The oligomers studied in a PMMA environment also exhibited short bursts of fluorescence, but the transition between on and off states tends to be more gradual. Intensity trajectories for oligomers in a PMMA matrix are found in Figure 3. The intensity trajectories for molecules on/in PMMA were intermediate between the OTS dynamics and the PEO dynamics but bore a stronger resemblance to the PEO dynamics. For molecules investigated in PMMA and PEO environments, the dynamics were indistinguishable for oligomers spin cast on top of spin-coated polymer films and for films spin cast from mixtures of the polymer and oligomer. We believe that this is due to the molecules experiencing similar environments in each sample preparation method, because the oligomers become partially embedded in the polymer matrixes when spin cast on top of them because of the slight solubility of PEO and PMMA in toluene, the SM casting solvent.

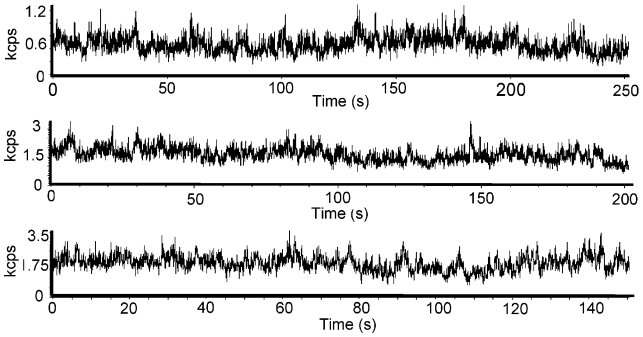

Figure 3. Intensity trajectories for three different single 5OPV molecules in a PMMA environment.

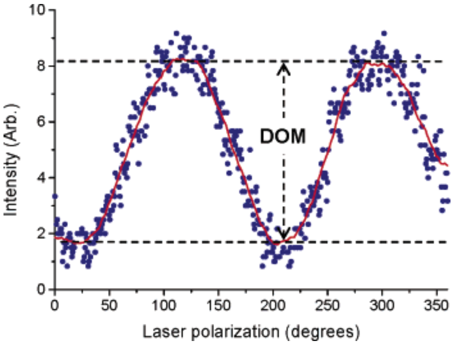

Figure 4. Illustration of the depth of modulation (DOM) for polarization modulation data obtained from a highly anisotropic single 5OPV molecule on glass (polarization modulation signal averaged over 50 s).

Polarization Modulation Data. The excitation laser polarization was modulated to produce rotating linearly polarized light at a fixed frequency, in accordance with our previous polarization modulation (PM) study on these molecules,[18] for all SM intensity trajectories obtained for this study. However, molecules in the PMMA and PEO environments spent so much time in an off state or exhibited a fluctuating dipole orientation in the $x-y$ plane because of increased freedom of motion in these environments that a PM statistical analysis could not be performed for these oligomers. Oligomers adsorbed to OTS monolayers did exhibit signals suitable for polarization modulation analysis, so we can compare the polarization modulation data for molecules adsorbed to glass to the data we obtained for molecules adsorbed to the less rigid OTS surface.

A single molecule's depth of modulation (DOM) is a measure of its excitation polarization anisotropy; it is the amplitude of its luminescence intensity as a function of a sweep of the excitation laser polarization orientation normal to the substrate through 180 degrees (DOM = $(I_{\max} - I_{\min})/I_{\text{ave}}$ where $I_{\max}$, $I_{\min}$, and I_{ave} are the background-corrected peak, trough, and average photon counts, respectively).[18] Figure 4 shows the polarization modulation taken from a single OPV molecule adsorbed to glass with a large DOM, indicative of an extended conformation. Figure 5a is a histogram of the depths of modulation for ~75 single 5OPV molecules adsorbed to glass. Figure 5b shows a DOM histogram generated for ~50 single 5OPV molecules adsorbed to OTS. Since all 5OPV samples were prepared from the same synthetic batch and were stored in the dark, the distribution of isomers, as determined previously by gas-phase ion mobility,[18] should be similar for both environments. The DOM histograms show a marked difference at low intensity between oligomers on glass and oligomers on OTS. On OTS,

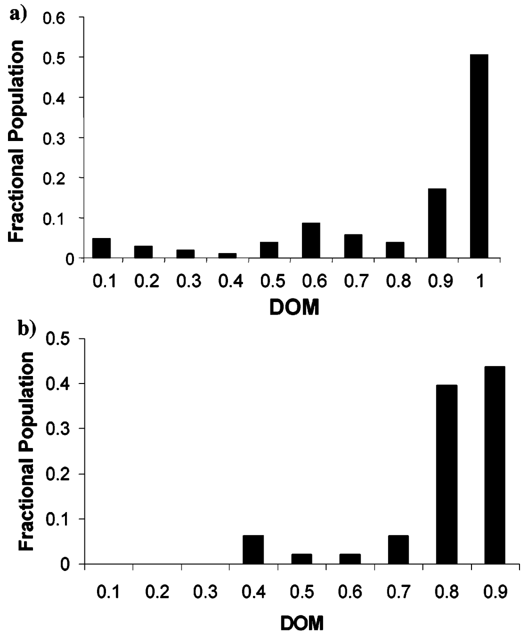

Figure 5. Histograms of the depth of modulation of single 5OPV adsorbed to (a) glass and (b) OTS. Note the lack of isotropic molecules in the OTS case.

we see little evidence of the most isotropic molecules. In the previous article, it was demonstrated that the most isotropic molecules are the molecules containing the most *cis*-vinylene defects.[18] To compensate for the steric effects introduced by a cis defect, a torsion angle between neighboring phenyl groups is a competing factor with conjugation in ground-state stabilization.[27,28] In a nonrigid environment, twisting motions about the C−C vinylene bonds provide a nonradiative pathway for excited-state energy, and cis defects promote nonplanar and therefore nonconjugated molecular conformations.[27] A >40° torsion angle has theoretically been determined to be a break in conjugation.[27,29] A break in conjugation in the middle of a 5OPV or 6OPV molecule will render the molecule nonluminescent at the excitation wavelength of 457 nm, because 457 nm is not absorbed by a two or three phenyl OPV chromophore. OTS provides a less rigid environment than glass, and it is very likely that we do not observe fluorescence from the most kinked molecules on OTS because of efficient nonradiative mechanisms. This agrees well with the negligent quantum yield in less rigid media of *cis*-stilbene compared to *trans*-stilbene. On average, the ratio of SM fluorescence intensity to laser excitation power appears lower for molecules adsorbed to OTS than for molecules adsorbed to glass, implying that the fluorescence quantum yield is lower for the OPV molecules adsorbed to OTS (as well as PMMA and PEO). This is analogous to the *cis*- and *trans*-stilbene results showing decreased fluorescence quantum yields with decreasing environmental rigidity.

Discussion

Physical versus Chemical Effects on Single Molecule Photophysics. In previous SM studies, the polarizability of the surrounding medium played a significant role in altering single molecule fluorescence behavior. For molecules with near unity quantum yields under varying conditions, the fluctuating dielectric of the medium surrounding single dye molecules can effectively be probed.[9,30] For OPV molecules, it is possible that changes in the polarizability of the surroundings yield changes in the emissive quantum yield (often measured as the single dye molecule radiative lifetime: $\tau \approx k_F^{-1}$), but here we are more concerned with the long-lived environment-induced changes seen in the intensity trajectories. Because the OPV molecules do not have a permanent dipole moment or exhibit a charge-transfer spectrum, differences in polarity among the environments studied are not expected to play as significant a role on the SM photophysics as seen for other polar single molecules.[5,7−9] Instead, we postulate that the fluctuations we see are linked to the viscoelastic properties of the surroundings, which are related to the longer time scale motions of the atoms and bonds of the matrix and which determine how much freedom of motion is afforded to the OPV single molecules. Single molecule dynamics caused by photoisomerization have previously been observed for the well-studied "Cy5" cyanine dye in fluid solution, where solvent viscosity was linked to photoisomerization.[31] Cis−trans photoisomerization is also related to the environmental sensitivity of another recently synthesized SM chromophore.[13]

Table 1. Elastic Moduli

material	elastic modulus (GPa)
glass (SiO_2)	~94[34]
OTS	6.2−12.4[35−37]
PMMA	1.8−3.1[38]
PEO	~0.3[39]

To attribute the trend in SM dynamics to the physical properties of the surrounding matrix, it is helpful to establish a basis of comparison of rigidity or viscoelasticity among the matrixes used. In solution fluorescence experiments, solvent viscosity is used to define rigidity. One measure of the rigidity of solids is the elastic modulus of a material. A table of literature values for the bulk elastic moduli of the materials used as SM environments is presented in Table 1. Although the elastic modulus is expected to differ from the bulk value for thin polymer films and we expect heterogeneity at the molecular level, these bulk moduli give us a useful starting point for comparing the mechanical properties of the materials. We also consider the qualitative factors associated with the rigidity of each matrix. Annealed, close-packed self-assembled monolayers of octadecyltrioxysilane are highly ordered and are therefore quasi-crystalline.[32] Consequently, even though this substrate is comprised of long "floppy" alkyl chains, it is actually quite rigid since the close packing severely restricts the motion of the chains.[32] For the polymer environments, we use the glass-transition temperature (T_g) as a basis of qualitative comparison of the mechanical properties of PMMA versus PEO. Above T_g, polymer molecules tend to be more mobile and the entire material tends to be less viscous than in the glassy phase. At room temperature, PMMA is well below its T_g (~90 °C) and

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[26] Sirbuly, D. J.; Schmidt, J. P.; Mason, M. D.; Summers, M. A.; Buratto, S. K. *Rev. Sci. Instrum.* **2003**, *74*, 4366−4368.

[27] Claudio, G. C.; Bittner, E. R. *Chem. Phys.* **2002**, *276*, 81−91.

[28] Kwasniewski, S. P.; Francois, J. P.; Deleuze, M. S. *J. Phys. Chem. A* **2003**, *107*, 5168−5180.

[29] Bredas, J. L.; Street, G. B.; Themans, B.; Andre, J. M. *J. Chem. Phys.* **1985**, *83*, 1323−1329.

[30] Tomczak, N.; Vallee, R. A. L.; van Dijk, E. M. H. P.; Garcia-Parajo, M.; Kuipers, L.; van Hulst, N. F.; Vancso, G. J. *Eur. Polym. J.* **2004**, *40*, 1001−1011.

[31] Widengren, J.; Schwille, P. *J. Phys. Chem. A* **2000**, *104*, 6416−6428.

[32] Britt, D. W.; Hlady, V. *J. Colloid Interface Sci.* **1996**, *178*, 775−784.

PEO is well above its T_g (∼−67 °C); therefore, we expect PMMA to be the more viscous of the two polymers. We expect that even with changes in polymer mechanical properties[33] because of the very thin films used in this study (∼50−100 nm), PEO should still provide the most fluid environment of all matrixes studied.

Another mechanism to consider for SM fluorescence intermittency is radical or polaron formation, as described by Orrit and co-workers and proposed as a model for the long-lived fluorescence quenching seen in single molecule intensity trajectories.[40−42] In this model, charge transfer to the surroundings is reversible up to a millisecond or longer, with the most polar surroundings supporting the longest oxidized times.[41] It is difficult to apply this model to the trend we observe, however, because OTS, the least polar environment studied, supports the longest off states for OPV single molecules, while PEO, the most polar environment, yields the shortest off times. While this is not exclusive proof that polaron formation does not occur, it does not seem to be the dominant mechanism for fluorescence intermittency.

We also consider the role of oxidizing contaminant molecules such as O_2 or H_2O.[14] Our experience with performing single molecule spectroscopy on OPV molecules in air is that rapid and irreversible photobleaching is inevitable, and only the most careful sample chamber preparation (with long pump−purge cycles) yields useful SM trajectory lifetimes (>∼30 s). For all environments in this study, any shortcoming in the preparation process was easily detected by rapid, irreversible SM bleaching. Therefore, oxygen or air molecules are probably not involved in any of the reversible on−off cycling seen in the OPV SM intensity trajectories. Significantly, however, these recently proposed photooxidation mechanisms do provide an explanation for the static fluorescence trajectories seen for OPV molecules supported on rigid substrates in purified N_2 conditions, which is in contrast to the blinking usually seen for multichromophoric PPVs. If electron transfer from neighboring polymer excitons can restore the oxidized (hole polaron) emissive chromophores to a neutral state, then the irreversible photooxidation is simply a consequence of the single chromophore nature of the OPVs.[42] Considering the lack of blinking in our glass-supported OPV SMs, the relative absence of blinking from PPV-based SMs cast from “good solvents” may similarly be due to lack of electron transfer caused by the decreased interchromophore interactions of these molecules because of their more extended chain conformations.[12,43]

Conclusions

An increase in molecular freedom of motion most likely involving torsional twisting about the vinylene bond leads to an increase in the on/off blinking behavior of phenylene-vinylene-based chromophores. Our study highlights the importance of considering conformational freedom as a possible mechanism for the long-lived or metastable off states observed for widely studied PPV derivatives such as MEH−PPV and other nonrigid molecules.[12−14,43,44] Temperature and chain-length dependence of the trend we have established in this article could lead to a better understanding of the thermodynamics of the on−off transitions we observe here, and time-resolved luminescence could aid in understanding the kinetics and quantum yield implications.

As many groups have demonstrated, the inorganic−organic interface is crucial to the operation of organic devices.[45,46] Single molecule spectroscopy provides a unique opportunity to study the effect of an interface on an organic material, one molecule or chromophore at a time. Our results suggest that the rigidity of the substrate or the mechanical properties of interface layers influence the morphology of the molecules in contact with the interface, which has important consequences for the flow of charge in real devices. This work also demonstrates that for PPV-based materials used in organic electronic devices, the viscoelastic properties of the materials should be considered when designing new molecules or blending strategies.

We have shown that the fluorescence intermittency of single oligo(phenylenevinylene) molecules strongly correlates to the structural rigidity of the environment. This result is in excellent agreement with earlier observations of stilbene, a two phenyl analogue of the oligo(phenylenevinylene) molecules. The dramatic effect of environmental rigidity on Φ_F of the stilbenes is well characterized and is related to fluorescence deactivation through twisting about the central C=C double bond. Likewise, we relate oligo(phenylenevinylene) single molecule fluorescence to the degree of conformational freedom afforded by the environment. As the rigidity of a single OPV molecule’s environment decreases, we observe its fluorescence tune from entirely on with no intermittency (glass) to blinking on a seconds time scale (OTS) to rapid sub-millisecond blinking (poly(ethylene oxide)). This dramatic shift in the behavior of one molecular species is unprecedented and demonstrates how important the physical surroundings can be in determining luminescence efficiency.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(33) Schonherr, H.; Frank, C. W. *Macromolecules* **2003**, *36*, 1188−1198.
(34) Oliver, W. C.; Pharr, G. M. *J. Mater. Res.* **1992**, *7*, 1564−1583.
(35) Barrena, E.; Ocal, C.; Salmeron, M. *J. Chem. Phys.* **1999**, *111*, 9797−9802.
(36) Barrena, E.; Kopta, S.; Ogletree, D. F.; Charych, D. H.; Salmeron, M. *Phys. Rev. Lett.* **1999**, *82*, 2880−2883.
(37) Weihs, T. P.; Nawaz, Z.; Jarvis, S. P.; Pethica, J. B. *Appl. Phys. Lett.* **1991**, *59*, 3536−3538.
(38) van Krevelen, D. W. *Properties of Polymers*; Elsevier: Amsterdam, 1990.
(39) Geng, H. Z.; Rosen, R.; Zheng, B.; Shimoda, H.; Fleming, L.; Liu, J.; Zhou, O. *Adv. Mater.* **2002**, *14*, 1387−1390.
(40) Zondervan, R.; Kulzer, F.; Orlinskii, S. B.; Orrit, M. *J. Phys. Chem. A* **2003**, *107*, 6770−6776.
(41) Zondervan, R.; Kulzer, F.; Kol’chenko, M. A.; Orrit, M. *J. Phys. Chem. A* **2004**, *108*, 1657−1665.
(42) Park, S. J.; Gesquiere, A. J.; Yu, J.; Barbara, P. F. *J. Am. Chem. Soc.* **2004**, *126*, 4116−4117.
(43) Huser, T.; Yan, M.; Rothberg, L. J. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 11187−11191.
(44) Ye, J. Y.; Ishikawa, M.; Yogi, O.; Okada, T.; Maruyama, Y. *Chem. Phys. Lett.* **1998**, *288*, 885−890.
(45) Salleo, A.; Chabinyc, M. L.; Yang, M. S.; Street, R. A. *Appl. Phys. Lett.* **2002**, *81*, 4383−4385.
(46) Salaneck, W. R.; Fahlman, M. *J. Mater. Res.* **2004**, *19*, 1917−1923.