JOURNAL OF CHEMICAL PHYSICS VOLUME 114, NUMBER 8 22 FEBRUARY 2001

Observation of multiple step de-excitation in luminescent single conjugated polymers

J. D. White, J. H. Hsu, Shu-Chun Yang, and W. S. Fann
Institute of Atomic and Molecular Science, Academia Sinica and Department of Physics, National Taiwan University, P. O. Box 23-166, Taipei, Taiwan, Republic of China

G. Y. Pern and S. A. Chen
Department of Chemical Engineering, National Tsing Hwa University, Hsinchu, Taiwan, Republic of China

(Received 11 October 2000; accepted 4 December 2000)

The fluorescence intensity fluctuation and polarization modulation of spin-cast single fluorescent conjugated polymers of 2,5-dioctyloxy p-phenylene vinylene (DOO-PPV) with length of the order of the persistence length have been studied. The results indicate that this type of polymer behaves like a collection of semi-independent excitons, with dipoles aligned predominately in the same direction. This suggests that this type of polymer can be considered as a linearly extended rigid structure (i.e., a straight rod). The fluorescent transient exhibits a multiple-step-like behavior with the count rate at each step being a multiple of a common step-size. The fluorescence variation follows the excitation polarization with a DC background observable in some molecules. This DC background indicates that the chromophores in some polymers are not aligned in the same direction. Variations in the Huang–Rhys factor at a single polymer level are also observed. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1343874]

I. INTRODUCTION

Organic thin-film electroluminescence based on conjugated polymers has recently been the focus of extensive research.[1] However, the basic photophysics of these materials is still not fully understood. Recent improvements in fluorescence microscopy techniques have made photophysics studies at the single molecule level possible.[2,3] Barbara's group has led the way in studying the photophysics of single PPV-PPyV and MEH-PPV polymers.[4–7] This paper presents the fluorescence intensity fluctuation of single DOO-PPV polymers [structure shown in the inset of Fig. 1(a)]. In contrast to previous work on long-chain MEH-PPV (~100 nm), the chain length of the DOO-PPV polymer used in this experiment, ~18 nm, is chosen to be close to its persistent length. {Although the persistence length of DOO-PPV has not been measured directly, the persistence length of poly[2-methoxy, 5-(2′-ethyl-hexyloxy-p-phenylene-vinylene] (BEH-PPV), a chain isomer, has been determined by light scattering to be ~11 nm (Ref. 8).} One would expect such a short-chain polymer to exhibit rodlike behavior both in solution and when spin-cast. In the work presented here, the dipole moment behavior on the single polymer chain is observed and analyzed. Variations of the Huang–Rhys factor at the single polymer level are also observed.

II. EXPERIMENTS

While the method for preparing dye molecules on substrate for single molecule experiment is well-documented,[9] the situation is completely different for polymers. Unlike small molecules, which are relatively easy to disperse in solvent and then spin-cast onto a substrate, polymers tend to aggregate together. The situation is particularly severe for polymer deposited in solid state thin film form, where interchain interactions can strongly influence the light emission.[10] As the present experiment requires a uniform chain length conjugated polymer to be dispersed in a thin nonconjugated matrix, we developed a novel method, ''sorting by solubility control'' to prepare such a polymer.[11] In this method, the variation of solubility with molecular weight and temperature is employed to obtain a polymer of a desired chain length. For the polymer used in this experiment, pristine DOO-PPV was first dissolved in 0 °C toluene.[12,13] After a few hours, nondissolved polymers were filtered out. After rinsing the residual powder, the procedure was repeated with chloroform, first at 0 °C and then at 24 °C. The 24 °C chloroform solution was dried by N_2 bubbling to obtain a final sample having a molecular weight (M_n) of 8600, and polydiversity (M_w/M_n) of 2.23 (determined by gel permeation chromatography). This corresponds to a polymer of 34 monomer units [determined by $(M_n M_w)^{1/2}$] having a relatively narrow chain length distribution (polymer length ~18 nm). The dispersed single-molecule (10^{-4} M of monomer) stock solution after further dilution (by a factor of 10^3–10^6) in the polystyrene matrix (polystyrene:chloroform:toluene =10 mg:18 ml:4 ml) was spin-cast (15 s at 2000 rps followed by 10 s at 3000 rps) onto a fused silica cover slip substrate (Esco Products). The resulting film thickness is <100 nm. Under these conditions, most molecules will align to have the polymer parallel to the plane. However, the plane of the chromophore, which is the same direction of the plane of the benzene ring, may lie in or out of the substrate plane.

The polymer was viewed on a homemade sample scanning confocal microscope consisting of a Nikon (Ellipse 660) optical microscope fitted over a standard AFM head (Park Scientific Instruments). The Z-control of the scanner

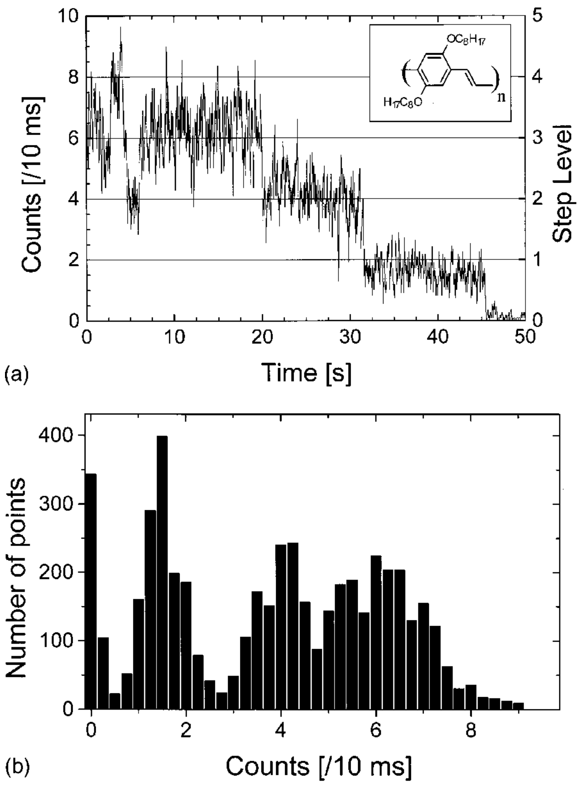

FIG. 1. Fluorescent transient (a) and histogram (b) of a single DOO-PPV molecule under low irradiance excitation (200 W/cm^2) with linearly polarized light. Four levels of approximately 2 counts/10 ms interval are visible. Due to the low excitation irradiance, signal to noise ratio has been increased by continuous averaging of 10 adjacent bins (this figure only). There are ~20 molecules/100 μm^2. Care has been taken to prevent exposure to oxygen and water during sample preparation and scanning. The chemical structure of DOO-PPV is shown in the inset.

electronics was disabled and the facedown sample scanned in the $X-Y$ plane. Laser excitation from the TEM$_{00}$ mode of a linearly polarized Ar-ion laser (488 nm), after attenuation and passing through a narrow band filter (Omega Optical) was reflected down to the sample by a dichroic beam splitter (Omega Optical). The size of the beam was chosen to slightly underfill the back of the objective (Nikon 100X oil immersion, N.A.$=$1.3, infinite focus) to minimize self-fluorescence from the objective. The fluorescence signal, collected through the same objective, after passing through a long pass filter was either sent to an APD (EG&G SPCM-AQ-131) for fluorescence intensity detection, or a spectrograph and CCD system (Acton Research 0.25 M and Princeton Instruments) to record the spectrum. For fluorescence intensity detection, a bandpass filter was used to reject residual excitation before the fluorescence was focused onto a 200 μm diam optical fiber. Upon exiting the fiber, the light was refocused onto an APD operating in photon counting mode. A 10 ms time constant (with 2 ms downtime) was used during experiments. For recording the fluorescence spectra, light was sent into a spectrograph and liquid N$_2$ cooled CCD system through optical fiber.

As quenching in conjugated polymers of this type is primarily a result of contamination from oxygen, the following steps were undertaken to limit the exposure of the solution and thin film to air.[4,5,14] Prior to spin-casting, dry-N$_2$ was bubbled through the solution to purge dissolved oxygen from the solution. The cleaned cover glass slips were placed in a dry nitrogen box (equipped with special filters for O$_2$ and H$_2$O) for a minimum of 2 h. Although the spin-coating process itself was performed in air, immediately after coating, the prepared sample was returned to the above chamber. Within the chamber the cover glass affixed to a specially designed holder to ensure that the film came into contact only with dry N$_2$. During image taking, the whole assembly was transferred to the scanner. Between scans, the sample was returned to the dry-N$_2$ box.

After a fast low irradiance scan to determine the position of polymers, individual molecules were systematically positioned at the focal point of the objective lens and their fluorescent transient recorded. The nature of this transient indicates whether the quenching of the polymer has single or multistep characteristics. The photoluminescence spectrum was also obtained at the same time. In addition, the nature (direction) of the absorption dipoles (μ) were investigated by slowly rotating (2.5 Hz) the linearly polarized excitation light (absorption and thus fluorescence being proportional to $|\mu \cdot E|^2$, where E is electric field vector).[15] In all cases linearly polarized light was used for excitation. With the exception of those experiments in which the direction of polarization was explicitly rotated, the direction of polarization was kept constant.

III. RESULTS

The fluorescence time decay from single DOO-PPV polymers was observed for a hundred molecules. Three molecules, representative of the three types of observed behavior, are shown in Figs. 1 and 2. Referring first to Fig. 1(a), taken at a relatively low excitation irradiance, fluorescence is seen to occur at discrete intensity levels separated by a step size of 2 counts/10 ms. After 5 s of bouncing between levels (level 3→4→2→3), the output intensity gradually reduces in a stair like fashion (level 3→2→1→0) with a much longer time constant (~10 s). For the 20 molecules studied at this excitation irradiance (200 W/cm^2), the step size was 3.5±1.5 counts/10 ms. Due to the low excitation irradiance, signal to noise ratio has been increased by continuous averaging of 10 adjacent bins (this figure only). Note that the abrupt changes at the step edge occur within the 10 ms time-resolution for the raw data. The corresponding intensity histogram of Fig. 1(a) is shown in Fig. 1(b). This steplike behavior is very different both from the exponential decay that one would expect for an ensemble of molecules and the single-step photobleaching that is observed in a single small molecule.[16]

In Fig. 2(a), an increase in excitation irradiance (1600 W/cm^2) is accompanied by a similar increase in count rate. The corresponding intensity histogram is shown in Fig. 2(b). For the 60 molecules studied at this excitation level, fluorescence occurred at discrete intensity levels separated by a step size of 45±15 counts/10 ms. Similar time-dependent fluorescence intensity jumping from level to level (level 7→4→6 →3→1→0) is observed. But, in contrast to the previous case, some steps are missed. There appears to be coordination being demonstrated between adjacent chromophores.

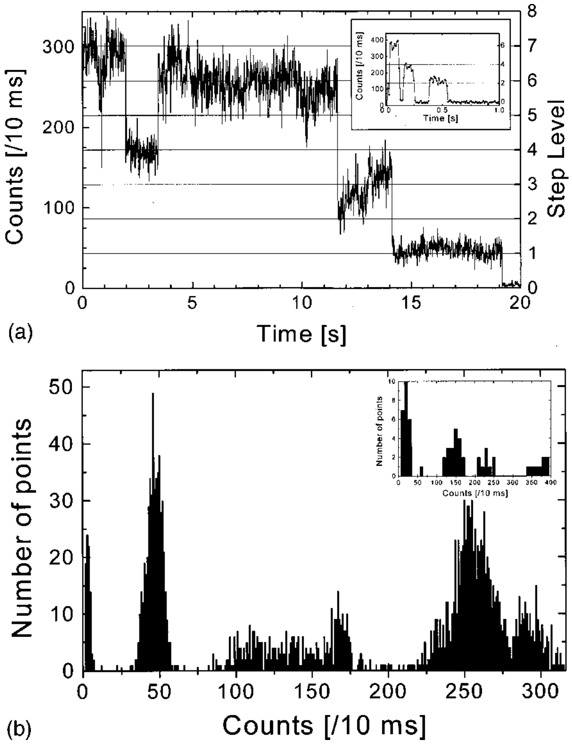

FIG. 2. Fluorescent transient (a) and histogram (b) of a single DOO-PPV molecule under high irradiance excitation (1600 W/cm^2) with linearly polarized light. While in the main figure, care has been taken to prevent exposure to oxygen and water during sample preparation and scanning, the inset shows the drastic effect of atmospheric exposure on sample lifetime. In the main figure, there are ~20 molecules/100 μm^2, while in the inset the coverage is ~2 molecules/100 μm^2. No averaging has been done in (a). For the histograms, 5 point continuous averaging has been employed in the main figure and 10 count binning for the inset.

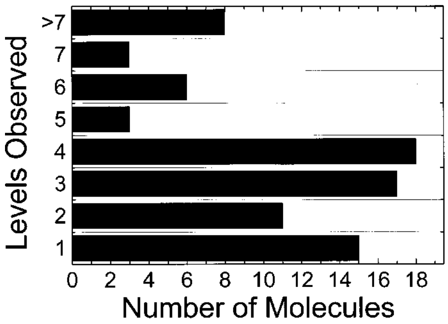

FIG. 3. Number of discrete fluorescence levels observed for 91 molecules. Data used in this assessment were taken with sample dilutions of 20 molecules/100 μm^2, 20 molecules/1000 μm^2, and 2 molecules/1000 μm^2. No significant difference was seen between data taken at the various sample dilutions. Due to the photon flux experienced by the molecules prior to recording, the number of steps per molecules may be biased towards the low side.

The inset of Fig. 2 displays a molecule for which no special efforts have been made to protect it from the atmosphere. The most obvious difference between those molecules studied in a N_2 environment and those studied under atmospheric conditions is the greatly reduced bleaching time—which at times makes the observation of individual steps difficult. While the first two molecules reflect the majority of cases, the polymer shown in the inset represents a type of behavior that is relatively unique (<10% of all molecules) in that it exhibits not only coordination within various parts of the system but also coordination across the entire molecule. The fluorescence transient exhibits jumping between levels while returning to zero in between (level $6 \rightarrow 0 \rightarrow 4 \rightarrow 0 \rightarrow 2 \rightarrow 0$ or level $3 \rightarrow 0 \rightarrow 2 \rightarrow 0 \rightarrow 1 \rightarrow 0$ depending on the count rate assigned to the base step). Taking these three types of molecules into consideration, it appears that while there may be strong communication along the chain, each section is also capable of individual behavior. The quenching behaviors of emitters do not always act independently. In a small molecule, intensity fluctuation that does not drop to zero is attributed to either spectral diffusion or rotational jumping.[15,17] The equal steps observed in Figs. 1 and 2 make either explanation improbable from this type of polymer. It should be noted that no significant behavioral difference—other than time-scale—was observed between those molecules isolated in an N_2 environment and those exposed to atmospheric conditions.

Similar fluorescent transients were observed for approximately 100 molecules. For each molecule, the number of discrete steps of fluorescence (i.e., 4 in Fig. 1 and 7 in Fig. 2, molecules with an ambiguous number of steps were generally excluded) was noted and compiled into the form of a histogram (Fig. 3). The histogram clearly indicates the multilevel emission and photobleaching of an ensemble of single molecules. Summarizing, for a given molecule, in general the step size is constant, and, within experimental error, scales linearly with excitation power. This view is consistent with all the dipole moments of all the chromophores of a given polymer being aligned in the same direction.

In order to investigate more carefully the behavior of the dipole ensemble of a single polymer, an electro-optical modulator was used to slowly rotate (2.5 Hz) the linearly polarized excitation beam ($|\mu \cdot E|$ varies at 5 Hz). Although in the majority of cases, full modulation is observed, there are exceptions. Figure 4 shows the fluorescent transient of one such exception. Initially the fluorescence output is what

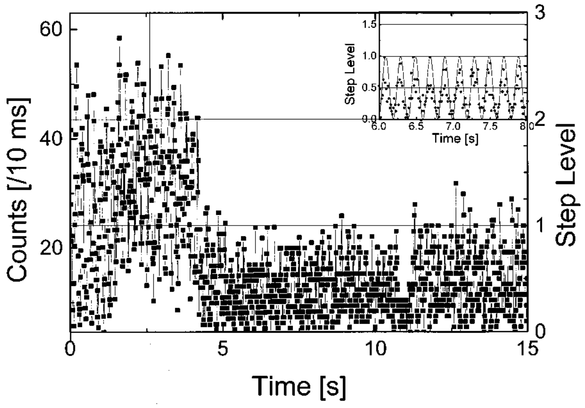

FIG. 4. Fluorescent transient of a single DOO-PPV molecule under high *irradiance* excitation with linearly polarized light. The direction of polarization is modulated at 2.5 Hz. Five distinct regions of emission (including dark state) are clearly visible (see text). Upper inset shows an example of curve fitting to the equation, $I = A \sin^2(\omega t + B) + C$ (see text).

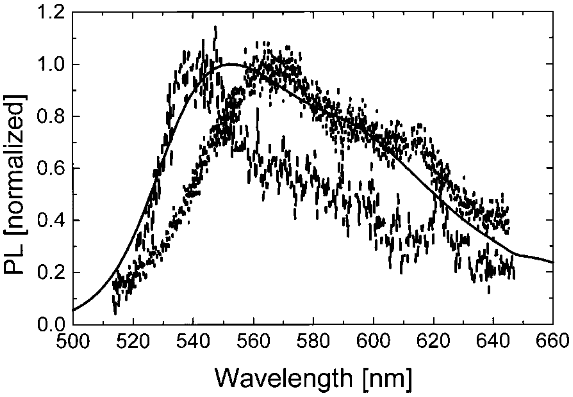

FIG. 5. PL emission spectra (··· and ---) from two single DOO-PPV polymers. The spectral width for both molecules is narrower than in chloroform (—). Each molecule exhibits significantly different spectral behavior.

TABLE I. The summarized results from the modulation experiment shown in Fig. 4. Each section of the curve was least squares fitted to the curve $I = A\sin^2(\omega t+B)+C$, where I is the fluorescence intensity, ω corresponds to the twice the frequency of modulation (5 Hz), and A, B, C are allowed to vary.

	Time (s)		Parameters		
Section	Start	Finish	$A(\pm 0.1)$	B	$C(\pm 0.1)$
1	0	1.3	1.9	−94°	0
2	1.3	4.2	1.3	−114°	0.8
3	4.2	10.7	1.0	+164°	0
4	10.7	11.2	0	···	···
5	11.2	23.0	1.0	−45°	0

would be expected for parallel dipoles—100% modulation of the fluorescence output. However, at ~1.3 s there is a sudden shift in phase. The fluorescence increases and a DC background appears. Note that the fluorescence intensity is *not* an integer multiple of the single step size. This continues until 4.2 s, when there is another sudden phase shift and the fluorescence drops to that expected for a single dipole or parallel dipoles. This continues with no phase change until the molecule goes dark (10.7 s). Emission starts again at 11.2 s with a different phase, and continues emitting with constant phase until at 23 s the molecule goes permanently dark.

The photoluminescence (PL) spectra from different single DOO-PPV polymers was taken at the same time as the polymer bleaching, as shown in Fig. 5. The fluorescence spectrum in chloroform solution is also shown for comparison. The fluorescence spectrum from a single DOO-PPV polymer is narrower because of the inhomogeneous effect of polymer in solution. Note that the shape of the fluorescence spectrum could be very different from one polymer to the other. This indicates that there is no single Huang–Rhys factor at the single polymer level. However, it does not exhibit distinctive two-state behavior, as in long chain MEH-PPV polymer.[7] The implication of these differences will be discussed in the next section.

IV. DISCUSSION

Differing orientations between chromophore dipoles (and hence absorption dipoles) and the incident electric field (i.e., $|\mathbf{u}\cdot\mathbf{E}|$ varies though ϑ) would be seen experimentally as a variation in step size. A constant step size thus implies that all dipoles maintain the same orientation with respect to the incident electric field. Clearly, this is the case for a single polymer (Figs. 1 and 2). In contrast, the variation in step-size seen between polymers (direction of E is kept constant) suggests that each polymer is oriented slightly differently with respect the electric field. The 30% variation between polymers suggests that the angle between $\mathbf{u}$ and $\mathbf{E}$, and hence the polymer orientation varies between 0 and 45° for the thin films investigated in this report. Thus there is correlation between chromophore orientation within a polymer, but there is only limited correlation between polymers in our thin films.

The results from the modulation experiment (Fig. 4) further confirm this view. In order to show that this result is consistent with a picture of four semi-independent chromophores, each with a fixed dipole moment (no rotation allowed), each section of the curve was least squares fitted to the curve $I = A\sin^2(\omega t+B)+C$, where I is the fluorescence intensity, ω corresponds to the frequency of modulation (2.5 Hz) and A, B, C are allowed to vary. The results of such a fit are summarized in Table I.

What is occurring in Secs. I, III, IV, and V is quite straightforward. In Sec. I, two parallel dipoles are emitting (chromophores a and b). In Sec. III, a single chromophore (c) is emitting. In Sec. V, a new chromophore (d), somewhere else in the polymer, starts to emit. In Sec. II, we propose that 3 chromophores (a, b, and c) are emitting. This can be seen from adding the output intensities incoherently,

$$\begin{aligned} I &= I_{A+B} + I_C \\ &= [1.9\sin^2(\omega t - 94) + 0] + [1.0\sin^2(\omega t + 164) + 0] \\ &= 1.1\sin^2(\omega t - 99) + 0.9, \end{aligned}$$

which, considering the noise level of the data, represents a reasonable fit.

Clearly, this is not the on–off or blinking behavior that has previously been observed for dye molecules or semiconductor nanocrystals where the entire system behaved as a single quantum system.[2] Rather it seems better to consider these larger polymers as an assembly of semi-independent chromophores on a rigid backbone. The polymer used is this experiment contains approximately 34 monomer units. It is reasonable to estimate the delocalization length to be approximately 6 monomers. We can thus picture the conjugated polymer used in this experiment as an assembly of 5–6 units that may act either individually or as a collective system. Due to the rigid backbone of conjugated polymers, dipoles of chromophores close to each other tend to ''line up'' and act as a single quantum system. As the distance between chromophore increases, the relative orientation of the dipoles becomes more random and their tendency to act coherently decreases. This clearly explains the observed multistep behavior (generally 4–5 distinct levels of fluorescence) and the nonzero DC photoluminescence background in some modulation experiments.

The present result clearly demonstrates multistep quenching, in contrast to previous work on PPV-PpyV and MEH-PPV in which at most 2 steps are seen before quenching.[4,5] Although the difference might be due to the chemical structure (DOO-PPV has symmetrical side groups while MEH-PPV has asymmetrical side groups), we believe *the difference in molecular weight, hence polymer length, should play the more significant role*. Persistence length is an important length scale for polymer conformation. When the polymer length is shorter or comparable to the persistence length, it tends to form rodlike structures. However, when the length is much longer than the persistence length, the situation is completely different. Homopolymers with weak basic unit interaction tend to form random coils in good solvent. Recently, Barbara's group has shown that neither the conventional random coil nor the rigid-rod is the preferred conformation for long conjugated polymers spin coated in matrix.[6] Their experimental results and simulation indicate that the ''defect cylinder,'' consisting of closely packed, parallel stiff chains, more accurately describes the conformation of long chain MEH-PPV in a polycarbonate matrix.[6]

In the experimental results presented here, the chain length of DOO-PPV is close to its persistence length and thus the conformation resembles a rigid rod. Related to Barbara's work, our results correspond to the limit in which there is only one stiff chain in the whole polymer. Since the short-chain DOO-PPV exhibits neither interruption nor bending, dipoles tend to align in one direction. Intrachain, $\pi-\pi$ interaction is thus almost nonexistent. Experimentally, this is seen in a sharply different fluorescence spectrum behavior in short-chain DOO-PPV and long-chain MEH-PPV. Because no intrachain aggregation is found in a rodlike polymer, the fluorescence spectrum only exhibits intrachain emission (seen as one distinct peak as in Fig. 5). In contrast, the long-chain MEH-PPV polymer has interchain interaction induced aggregation, so there exists both intrachain and aggregate emission—resulting in a single polymer fluorescence spectrum containing two rather than one distinctive peak.[7,18]

The defect-cylinder model also provides an explanation for the variation in dipole direction seen in some of the polarization experiments (Fig. 4). In this case, the change in dipole direction would be understood as the result of a tetrahedral chemical defect that causing a ''kink'' in an otherwise straight rigid rod.

V. CONCLUSION

In conclusion, the fluorescent transient of a single DOO-PPV polymer with molecular weight around 10 000, and length close to the persistence length, is not simply on/off blinking. Rather, multiple steps with generally equal spacing are observed. This suggests that this polymer can be considered to be composed of a number of closely coupled basic units that may act either cooperatively or independently, adjacent dipoles tending to orient in parallel and sometimes act together. Polymers with length close to the persistence length clearly maintain their rigid-rod structure when spin-cast.

ACKNOWLEDGMENTS

The gracious assistance of P. K. Wei, Wenchieh Yen, and Kuang Lang Ho during experiments is greatly appreciated. This research was supported by the National Science Research Council, Republic of China.

[1] R. H. Friend, R. W. Gymer, A. B. Holmes *et al.*, Nature (London) **397**, 121 (1999).
[2] M. Nirmal, B. O. Dabbousi, M. G. Bawendi, J. J. Macklin, J. K. Trautman, T. D. Harris, and L. E. Brus, Nature (London) **383**, 802 (1996).
[3] W. E. Moerner and M. Orrit, Science **283**, 1670 (1999).
[4] D. A. Vanden Bout, W. T. Yip, D. Hu, D. K. Fu, T. M. Swager, and P. F. Barbara, Science **277**, 1074 (1997).
[5] D. Hu, J. Yu, and P. F. Barbara, J. Am. Chem. Soc. **121**, 6936 (1999).
[6] D. Hu, J. Yu, K. Wong, B. Bagchi, P. J. Rossky, and P. F. Barbara, Nature (London) **405**, 1030 (2000).
[7] J. Yu, D. Hu, and P. F. Barbara, Science **289**, 1327 (2000).
[8] C. L. Gettinger, A. J. Heeger, J. M. Drake, and D. J. Pine, J. Chem. Phys. **101**, 1673 (1994).
[9] E. Betzig and R. J. Chichester, Science **262**, 1422 (1993).
[10] J. H. Hsu, W. Fann, P. H. Tsao, K. R. Chuang, and S. A. Chen, J. Phys. Chem. A **103**, 2375 (1999).
[11] J. H. Hsu (private communication).
[12] G. J. Sarnecki, P. L. Burn, A. Kraft, R. H. Friend, and A. B. Holmes, Synth. Met. **55–57**, 914 (1993).
[13] S. H. Askari, S. D. Rughooputh, and F. Wudl, Synth. Met. **29**, E129 (1989).
[14] M. Yan, L. J. Rothberg, F. Papadimitrakopoulos, M. E. Galvin, and T. M. Miller, Phys. Rev. Lett. **73**, 744 (1994).
[15] T. Ha, Th. Enderle, D. S. Chemla, P. R. Selvin, and S. Weiss, Phys. Rev. Lett. **77**, 3979 (1996).
[16] M. Wu, P. M. Goodwin, W. P. Ambrose, and R. A. Keller, J. Phys. Chem. **100**, 17406 (1996).
[17] H. P. Lu and X. S. Xie, Nature (London) **385**, 143 (1997).
[18] T. Huser, M. Yan, and L. J. Rothberg, Proc. Natl. Acad. Sci. USA **97**, 11187 (2000).