



ELSEVIER

Journal of Luminescence 98 (2002) 41–44

JOURNAL OF
LUMINESCENCE

www.elsevier.com/locate/jlumin

Single-molecule fluorescence of long-chain DOO-PPV conjugated polymers prepared by different oxygen reducing methods

Wen-Yu Sun^{a,b}, Jui-Hung Hsu^a, Shu-Chun Yang^{a,c}, J.D. White^a,
Wunshain Fann^{a,b,*}

^a*Institute of Atomic and Molecular Science, National Taiwan University, Academia Sinica, P.O. Box 23-166, Taipei, Taiwan, ROC*

^b*Department of Physics, National Taiwan University, Taipei, Taiwan, ROC*

^c*Department of Physics, Tamkang University, Taipei, Taiwan, ROC*

Abstract

Quenchers, such as oxygen, play an important role influencing the transient fluorescence behavior of conjugated polymers. It is important to reduce these quenching effects in order to study a polymer's intrinsic fluorescence behaviors. The fluorescent transient of a single DOO-PPV polymer embedded in a polystyrene matrix is found to be qualitatively dependent on the sealing method used to protect the thin film from contact with oxygen. The results show that the preparation process affects single polymer fluorescence. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Single molecule; Fluorescence; Conjugated polymer

1. Introduction

The behaviors of fluorescence fluctuations, such as the presence of “dark-states”, are heavily influenced by quenchers [1,2], such as oxygen in the vicinity of the conjugated polymer [3,4]. In order to understand how conformations influence the photo-physics of polymers, it is important to improve the sample protection technique to diminish the rate of oxygen quenching [5]. In

the absence of quenchers, the intrinsic fluorescent transient of single molecules can then be investigated.

In this study, the fluorescence transient of a single long-chain polymer protected by different methods is observed in order to optimize sample preparation and sealing. It is found that a buffer PMMA layer with an Al coating on the top provides both a high-count rate and long lifetime.

2. Experiment

Poly[2,5-dioctyloxy, *p*-phenylene-vinylene] (DOO-PPV) is a luminescent conjugated polymer with symmetric side groups. The chemical

*Corresponding author. Institute of Atomic and Molecular Science, National Taiwan University, Academia Sinica, P.O. Box 23-166, Taipei, Taiwan, ROC. Tel.: +886-2-223-620212; fax: +886-2-223-620200.

E-mail address: fann@gate.sinica.edu.tw (W. Fann).

structure is shown as inset in Fig. 4. The tetrahedral defects produced during synthetic process is low, $\sim 1\%$ (as measured by NMR using the technique of Becker et al. [6]). In this experiment, pristine DOO-PPV polymer powders are separated to different chain lengths by a novel method called “sorting by solubility control” [7]. First, the pristine DOO-PPV powders were dissolved in 0°C toluene. Secondly, un-dissolved powder was filtered out few hours later, and the process was repeated with chloroform [8] at 0°C , 24°C , and 40°C to separate out those polymers having a short chain length. Finally, the residual powder was dissolved in $> 50^\circ\text{C}$ chloroform solution. This high molecular weight component ($M_w \sim 1,000,000$) with a chain length longer than 300 excitons, was used in this study. After dilution into a polystyrene matrix (polystyrene:chloroform:toluene = 20 mg:16 ml:3 ml), the solution was spun-cast onto UV grade silica cover slips to obtain a ~ 100 nm thick conjugated polymer/polystyrene film.

As oxygen is one of the main quenchers for luminescent conjugated polymers, three different preparation processes were used to protect the films from exposure to atmospheric oxygen. The first sample was directly sealed in a nitrogen environment (glove box). For the second, a 200 nm thick layer of aluminum was evaporated directly on top of the film prior to sealing in the same nitrogen environment. Finally, in the third sample, a buffer layer PMMA was first spin-cast on top of the thin film. A 200 nm thick layer of aluminum was then evaporated on top of the PMMA layer prior to sealing in the same nitrogen environment. The samples were systematically observed under a homemade sample scanning confocal microscope modified from a Nikon (Ellipse 600) optical microscope (Fig. 1).

3. Results and discussion

After rapidly raster scanning the sample (Fig. 2 [inset] shows a typical photoluminescence image of a single polymer), the excitation beam was focused on a single polymer and the fluorescence transient observed. Typical fluorescent transients for poly-

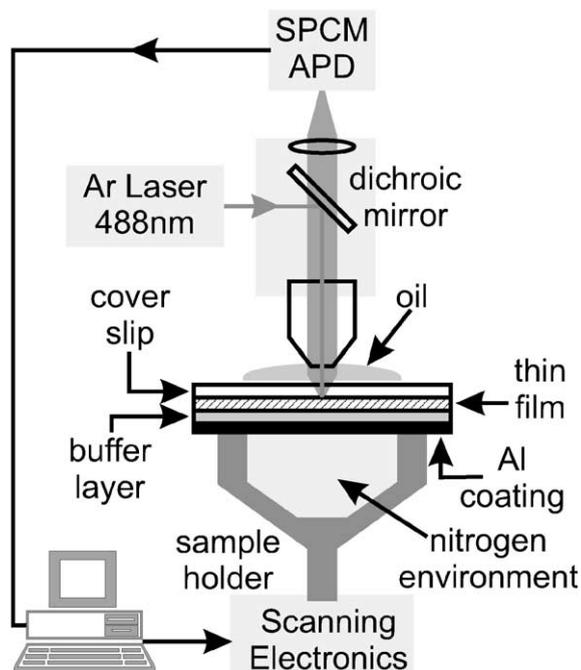


Fig. 1. Schematic of the sample scanning confocal microscope and nitrogen cell. Linearly polarized light from an Argon laser (488 nm) excited a single polymer, and the fluorescence collected by the same objective lens (Nikon 100X oil immersion, N.A. = 1.3, infinite focus) and detected by a single photon counting avalanche photo-diode detector. The DOO-PPV polymers are embedded in a polystyrene thin film protected by PMMA and Al coating. The sample is sealed in a sample holder filled with N_2 .

mers protected from oxygen using each of the previously mentioned methods are shown in Figs. 2–4, respectively. In the majority of cases, the fluorescence transient of single long-chain DOO-PPV polymers under all three sealing conditions is characterized by an exponential decay modulated with steps [9]. This is very different from the “ON/OFF” blinking observed in small molecules [10] and the distinct multiple-step quenching in single short-chain DOO-PPV polymers [11,12]. The exponential decay may be due to the effect of solvent [13], and the result implies that many excitons emitted light in the process. The fluorescence transient reflects the quenching behavior of quencher in a single polymer.

Fig. 2 is typical of the transient observed for those in which no Aluminum layer was deposited.

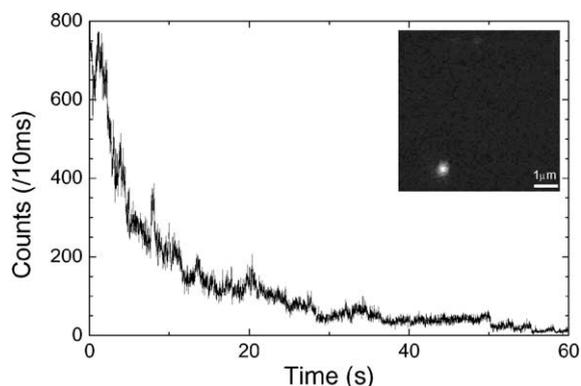


Fig. 2. Fluorescent time trace of a single long-chain DOO-PPV polymer sealed in a nitrogen environment. The exponential decay and many steps mix the fluorescence transient of single long-chain DOO-PPV polymers. Deep steps appear in the fluorescence transient before 5 s, but on a longer time interval exponential decay dominates. The inset shows a typical photoluminescence image of a single polymer obtained by raster scanning the excitation laser beam.

The fluorescence intensity decays very quickly and its lifetime was short. This result indicates that quench behavior is intense between polymer and quencher. The trace in Fig. 3 is representative of those samples in which an aluminum layer was directly coated onto the polystyrene film. Similar stepping behavior is seen. As mentioned above, in the majority of polymers observed there is both exponential decay and sudden intensity fluctuations. The key difference between those films covered with the aluminum coating and those without is the number of sudden *recoverable* intensity drops. In the aluminum-coated case, it is much more likely that the fluorescence intensity will recover after a sudden intensity drop. It is quite possible that these steps result from the existence of another quenching channel between polymer and Al layer (the polymer film is quite thin). (It should be noted that the affect of aluminum quenching would not be as readily observed in short-chain polymers due to the fact that emission is also a function of the relative orientation of the excitation and exciton dipoles. While the random orientation of the dipoles in long-chain polymers mitigate this effect, in short chain polymers the alignment of dipoles means

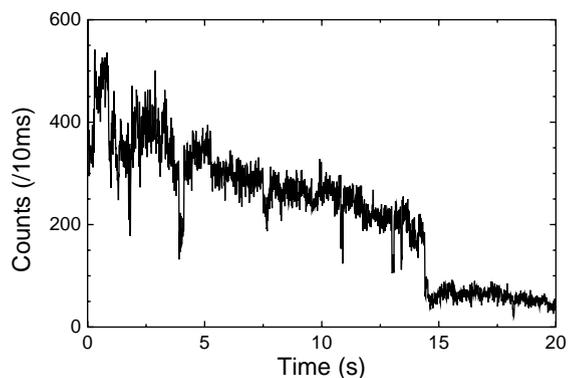


Fig. 3. First 20s of the fluorescent time trace of a single long-chain DOO-PPV polymer first protected by an aluminum layer and then sealed in a nitrogen environment. Recoverable intensity drops superimposed on an exponential decay characterize this trace.

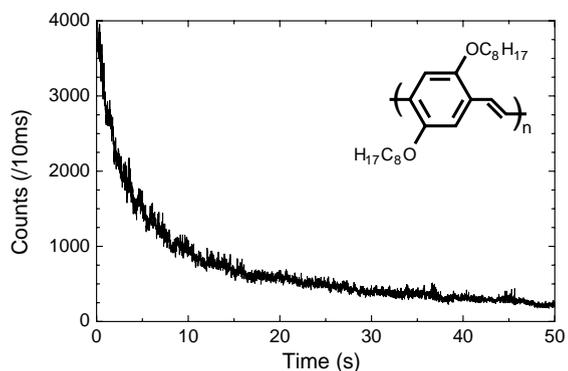


Fig. 4. Fluorescent time trace of a single long-chain DOO-PPV polymer protected by a PMMA film and then coated with an aluminum layer before being sealed in a nitrogen environment. Exponential decay dominates the fluorescent time trace. The inset shows the chemical structure of DOO-PPV.

that emission intensity varies greatly from polymer to polymer.)

Thus, in the final sample considered here, a PMMA layer was spin-cast on top of the polymer film before Al coating. Since PMMA is not conducting, the excitons on the polymer chain should not be quenched while the Al layer ensures that the prevention of oxygen is efficient. One representative result is shown in Fig. 4. Qualitatively, the decay of the fluorescent transient is again predominately exponential. It is quite similar to that observed for polymers sealed in N_2 without

any aluminum coating. Quantitatively, however, significantly higher fluorescence intensity and a significantly longer lifetime are exhibited for samples prepared with the PMMA buffer layer than either of the other processes. Note that the count-rate at 50 s is still well above the background noise which is ~ 3 counts/10 ms. Since the polymer film is both protected from oxygen and metal quenching, we conclude that exponential decay reflects the intrinsic photo-physics properties of long-chain DOO-PPV. Note that the above results do not provide a direct measurement of oxygen contents in different samples. We are currently engaged in measuring the oxygen content in the films utilizing DiI molecules and the technique of Barbara et al. [14].

4. Conclusion

In this paper, different methods were examined to find the optimized way to exclude oxygen influence in single polymer experiments. The fluorescent transient of a single polymer embedded in a thin film is found not only to be dependent on sample preparation [9] but also dependent on the sample sealing technique. Polymers embedded in films protected by both a PMMA film and an aluminum layer were found to exhibit the highest fluorescence intensity and longest lifetimes. The PMMA/Al combination thus provides the best

protection for a conjugated polymer from oxygen quenching.

Acknowledgements

We thank Prof. S.A. Chen's group in National Tsing-Hwa University for making the polymer powders and the referee's suggestions. This research is supported by the National Science Council and Ministry of Education in Taiwan.

References

- [1] D.A. Vanden Bout, et al., *Science* 277 (1997) 1074.
- [2] Ji Yu, et al., *Science* 289 (2000) 1327.
- [3] R. Jakubiak, et al., *J. Phys. Chem. A* 103 (1999) 2394.
- [4] T.Q. Nguyen, et al., *J. Chem. Phys.* 110 (1999) 4068.
- [5] D. Hu, et al., *Nature* 405 (2000) 1030.
- [6] H. Becker, et al., *Macromolecules* 32 (1999) 4925.
- [7] J.H. Hsu, private communication.
- [8] J.-J. Hsu, et al., *J. Phys. Chem. A* 103 (1999) 2375.
- [9] Shu-Chun Yang, private communication.
- [10] M. Wu, P.M. Goodwin, W.P. Ambrose, R.A. Keller, *J. Phys. Chem.* 100 (1996) 17406.
- [11] J.D. White, J.H. Hsu, S.-C. Yang, W.-S. Fann, G.Y. Pern, S.A. Chen, *J. Chem. Phys.* 14 (2001) 3848.
- [12] J.D. White, et al., *Chem. Phys. Lett.* 338 (2001) 263; J.D. White et al., at this special issue.
- [13] T. Huser, et al., *PNAS* 97 (2000) 11187.
- [14] D.S. English, A. Furube, P.F. Barbara, *Chem. Phys. Lett.* 324 (2000) 15.