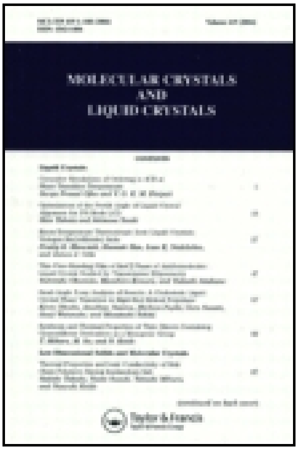

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Self-Assembled Polythiophene Monolayer on Gold Surface

Chong Kyu Shin [a] , Hoosung Lee [a] , Changsoo Jung [b] , Doseok Kim [b] & Bum Ku Rhee [b]

[a] Department of Chemistry, Sogang University, Seoul, 121-742, Korea

[b] Department of Physics, Sogang University, Seoul, 121-742, Korea

Version of record first published: 24 Sep 2006

To cite this article: Chong Kyu Shin, Hoosung Lee, Changsoo Jung, Doseok Kim & Bum Ku Rhee (2000): Self-Assembled Polythiophene Monolayer on Gold Surface, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 349:1, 167-170

To link to this article: http://dx.doi.org/10.1080/10587250008024891

Mol. Cryst. Liq. Cryst., 2000, Vol. 349, pp. 167-170
Reprints available directly from the publisher
Photocopying permitted by license only

Self-Assembled Polythiophene Monolayer on Gold Surface

CHONG KYU SHIN[a], HOOSUNG LEE[a], CHANGSOO JUNG[b], DOSEOK KIM[b] and BUM KU RHEE[b]

[a]*Department of Chemistry, Sogang University, Seoul, 121–742, Korea and*
[b]*Department of Physics, Sogang University, Seoul, 121–742, Korea*

Poly(3-dodecylthiophene) monolayer was self-assembled on the gold surface by immersion of gold substrate into the solution of polythiophene. The peak of the photoluminescence (PL) spectra of the monolayer sample was redshifted compared to those of a bulk polythiophene. By exciting the sample with linearly-polarized light incident obliquely to the sample, strong anisotropy in the fluorescence intensity was observed as the polarization direction of the pump beam was rotated. From this result, the tilt angle of the thiophene ring with respect to the surface normal of the gold substrate was measured.

INTRODUCTION

Since it was discovered that di-n-alkyl disulfides from solution adsorbed on gold surface and formed a monomolecular layer [1], the field of self-assembled monolayers (SAMs) has grown very rapidly and many different kinds of self-assembled systems have been found and investigated [2]. Especially, organic compounds containing sulfur are known to have a strong affinity to transition metal surfaces. To name just a few, the compounds known to form monolayers include alkyl sulfides and alkyl disulfides [1,2], thiophene oligomers [3], and thiophenols [4]. In this paper, we investigated the characteristics of self-assembled monolayer of poly-alkylthiophene on gold surface. Polythiophene is a well-known conducting polymer and has been investigated extensively for the potential applications to electronics such as polymer batteries and electrodes [5]. Recently, the self-assembly of poly(3-octylthiophene) on gold surface was first reported and some of its material properties were studied [6]. Here, we investigated the conformational information about the film from its photoluminescence properties.

EXPERIMETAL

Thin films of gold (100 nm) were prepared by thermal evaporation of gold onto glass substrate coated with indium tin oxide at pressures of less than 10^{-5} Torr. The synthesis and polymerization of poly(3-dodecylthiophene) was described elsewhere [7]. The polythiophene was dissolved in the solvents of dry-distilled chloroform, tetrahydrofuran, p-xylene, or toluene. Then the gold plate was immersed into these solutions of polythiophene (10 mM) for 24 hours at room temperature, followed by rinsing several times with fresh solvent and drying in a stream of nitrogen. Since repeated rinsing with the solvents above did not wash away the polymer, it was concluded the polythiophene was chemisorbed on gold in the form of a monolayer.

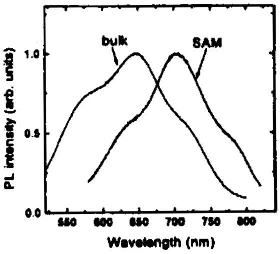

FIGURE 1 PL spectra of SAM and spin-cast polythiophene.

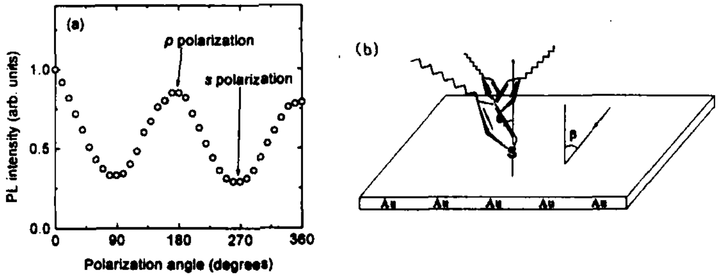

FIGURE 2 (a) PL intensity at the peak vs. input beam polarization. (b) picture of polythiophene SAM on gold substrate.

RESULTS AND DISCUSSION

Figure 1 shows the PL spectrum of the SAM and bulk polythiophene with excitation wavelength at 477 nm. Compared with the PL spectrum of the bulk (thick film) polythiophene shown as a comparison, the peak of SAM is redshifted by about ~60 nm. The shift of the PL spectrum between two samples of same chemical composition should be interpreted as the structural change of the polymer towards a longer conjugation length along the chain [7], so the chains of polythiophene in SAM are believed to be more relaxed.

Next PL was measured by illuminating the film with an incidence angle β=20° and rotating the polarization direction with respect to the incidence plane. The observed PL as shown in Fig. 2(a) is strongly anisotropic. We attempted to relate this result with the orientation of polythiophene on gold surface. The azimuthal orientation of the adsorbed molecules on gold substrate should be isotropic, however, the molecures will energetically prefer some polar orientation. By assuming the δ-function distribution for θ, the ratio of the amount of absorption by s- and p-polarized pump beam is

$$\frac{L_p}{L_s} = \frac{|1-r_p|^2}{|1+r_s|^2}\cos^2\beta + 2\frac{|1+r_p|^2}{|1+r_s|^2}\sin^2\beta\cot^2\theta \qquad (1)$$

where L_p and L_s are proportional to the square of total electric field at the surface, r_p and r_s are the Fresnel factors of air-gold interface with an incidence, and β and θ are as shown in Fig. 2(b). By fitting the data with the above equation, we were able to determine the tilt-angle to be about 23 degrees. For this analysis, we assumed the PL intensity of the sample is isotropic irrespective of the polarization of illuminating light, although fluorescence from anisotropically oriented molecules might not be uniform for all solid angles. Also, it should be reminded that small change in the refractive index of the gold substrate could yield quite different values for tilt-angle. More accurate method to determine the orientation of monolayer is being investigated.

D. Kim and B. K. Rhee acknowledge the financial support from the Basic Research Program of the KOSEF grant No. 19984027. H. Lee acknowledges the support of the Basic Science Research Institute Program of Ministry of Education (Project No. BSRI-99-3411), and the support of Korea Science and Engineering Foundation through the Center for Electro- and Photo-Responsive Molecules (CRM), Korea University.

References

[1] R. G. Nuzzo and D. L. Allara, *J. Am. Chem. Soc.* **105,** 4481 (1983).
[2] See, for example, A. Ulman, *Chem. Rev.* **96**, 1533 (1996).
[3] F. Garnier et al., *J. Am.Chem. Soc.* **115,** 8716 (1993).
[4] M. A. Bryant, S. L. Joa, J. E. Pemberton, *Langmuir* **9,** 753 (1992).
[5] B. Scrosati, *Applications of Electroactive Polymers* (Chapman & Hill, London. 1994).
[6] Z. Gao, K. S. Siow, and H. S. O. Chan, *Synthetic Metals* **75,** 5 (1995).
[7] P. Buvat and P. Hourquebie, *Macromolecules* **30,** 2685 (1997); M. Kobashi and H. Takeuchi, *Macromolecules* **31,** 7273 (1998).