

Highly Polarized Luminescence from Optical Quality Films of a Semiconducting Polymer Aligned within Oriented Mesoporous Silica

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Semiconducting polymers have received considerable attention for the preparation of electronic and optoelectronic devices due to their unique photophysical properties and solution processability.¹ These molecular semiconductors are intrinsically anisotropic in their intramolecular conductance and luminescence polarization, with both oriented along the polymer chain. However, traditional processing techniques lead to films with random orientations of chains in a wide variety of conformations, creating effectively isotropic materials. By controlling the conformation of individual polymer chains at the nanometer length scale, however, the intrinsic anisotropy of these electronic materials can be recovered.^{2–4} The ability to direct the orientation, conformation, and interactions of these nanoscale building blocks is the key element to this research.

One particularly important application is the ability to produce a uniform orientation of transition moments for both optical displays and the emerging field of molecular-scale optoelectronics.^{5,6} In this work, this goal is accomplished using well-oriented continuous films of 2D hexagonal mesoporous silica to align the semiconducting polymer, poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV).⁷ These films show a high level of transition moment orientation for the polymer and, importantly, are optically transparent and densely filled.

In general, self-assembled surfactant-templated mesoporous materials make for an attractive host for orientation due to both their physical attributes and their simple bottoms-up solution phase self-assembly process, which allows for a massively parallel synthesis.^{3,8} Host/guest interactions are highly tunable due to the multitude of framework materials, geometrical orders (lamellar, 2D or 3D hexagonal, and cubic), and pore sizes (2–20 nm) possible with mesoporous materials.⁹ One limitation of these materials as hosts, however, is that, although they are well ordered on the nanoscale, generally they do not show macroscopic ordering — individual micron-sized domains have random orientations within the material. Various attempts have been made to prepare uniaxial aligned silica mesochannels as bulk materials with some success.¹⁰ For example, magnetic field aligned mesoporous silica has been used as an oriented host for semiconducting polymers, but the production of these materials requires strong fields and they form a scattering solid that is unsuitable for some optical applications.³

The mesoporous films in this work are prepared on glass substrates coated with a rubbed polyimide. The mesoporous film is formed through a slow epitaxial growth of a self-organized mixture of hydrolyzed silicon alkoxide and the nonionic structure directing agent C₁₆H₃₃(OCH₂—CH₂)₁₀OH under acidic conditions.¹¹ The mesoporous silica forms continuous films, as viewed by optical microscopy, with well ordered *p6mm* 2D hexagonal structures. Upon drying and calcination to remove the surfactant template, the film shrinks normal to the substrate, resulting in a highly oriented

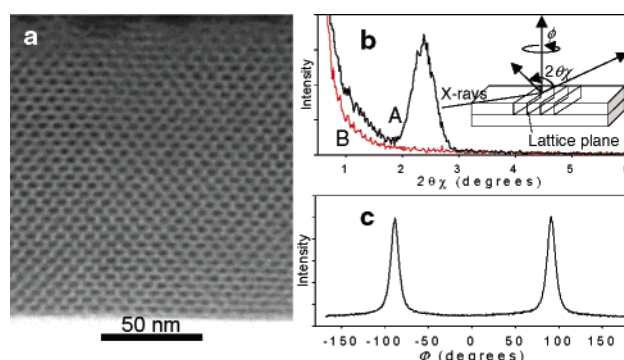


Figure 1. Structural characterization of the mesoporous silica thin film. (a) Cross-sectional STEM image of the mesoporous thin film after calcination and polymer incorporation. The sample was cut perpendicular to the alignment direction. Brighter areas are the silica framework; the bright band on the bottom is the substrate. (b) In-plane XRD demonstrates the uniaxial alignment of the mesochannels. (c) Pore alignment is further demonstrated by diffraction data obtained by rotating the sample about ϕ while holding $2\theta_\chi$ fixed at the peak from part (b). Peaks develop only when the mesochannels are aligned parallel to the incident beam.

and ordered 2d rectangular *cm̄m* structure, as demonstrated by cross-sectional scanning transmission electron microscopy (STEM) (Figure 1a) and both Bragg and in-plane X-ray diffraction (XRD) data (Figure 1b,c). The orientation of the mesopores is demonstrated by in-plane XRD (Figure 1b,c). In Figure 1b, trace A shows a peak when the mesochannels are aligned parallel to the incident X-rays, but no peak in trace B when the alignment is perpendicular. The angular distribution is shown in Figure 1c. Pore alignment is achieved through the interactions of the hydrophobic surfactant tails with the chains of the rubbed polyimide surface of the substrate. For these materials, the pore size of the calcined materials was estimated to be 48 Å based on a BJT fit to nitrogen desorption isotherms from concomitantly prepared powder samples.¹¹

After synthesis, the films are treated to incorporate MEH-PPV.³ After air calcination to remove the surfactant and polyimide, the hydrophilic silica mesopore surface is modified with either phenyldimethylchlorosilane or a 1:1 mix of trimethylchlorosilane and 1,1,1,3,3,3-hexamethyldisilazane to produce an organic surface coating. The silylated films are then soaked in a solution of MEH-PPV in chlorobenzene (molecular weight ~50k) at 80 °C for 24 h, followed by repeated rinses with chlorobenzene to remove any unincorporated polymer adhering to the surface.³

Polarized absorption data, Figure 2, indicates that the majority of the polymer is oriented in the direction of the mesochannels; the parallel/perpendicular absorption ratio is 4.9. Polymers absorbing parallel to the mesochannels are also slightly red-shifted as compared both to those absorbing perpendicular to the pores and to polymers in a spin cast film. Apparently, chains aligned with the pores are elongated and straight, leading to larger conjugation

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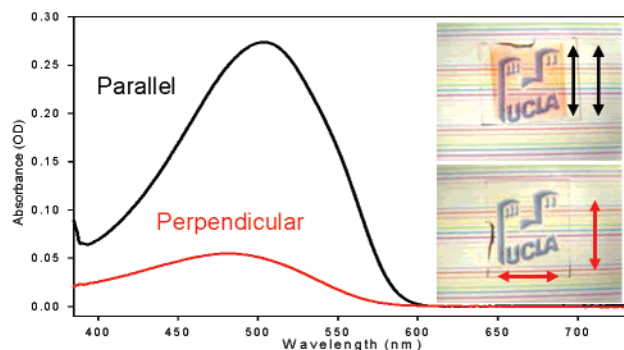


Figure 2. Polarized absorption from MEH-PPV in an aligned mesoporous silica film. The ratio of peak heights is 4.9. The pictures were taken with polarized back lighting to illustrate their optical transparency and alignment. The samples appear colored when the light polarization is parallel to the mesochannels, but clear when the polarization is perpendicular.

lengths and lower energy excited states. Any partly coiled or kinked chains would lead to perpendicular absorption.

Polarized fluorescence was obtained using 532 nm laser excitation and collecting with a linear CCD array spectrometer with no polarization dependence. Orientations of the sample, excitation, and emission polarizers are given with respect to the lab frame, as shown in the inset of Figure 3. As a standard, a rhodamine dye incorporated in poly(methyl methacrylate) gave a value of nearly 3, as expected for a random distribution of fixed transition dipoles; the small deviations from a value of 3 were used to generate an instrument correction function.

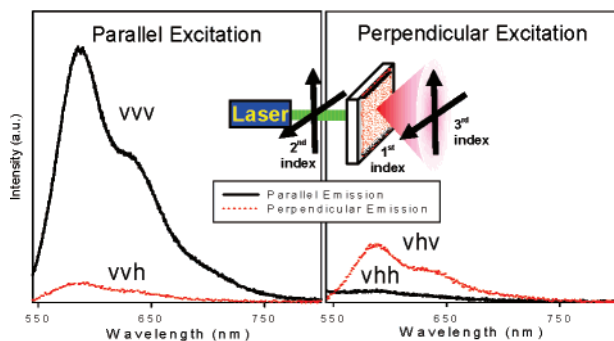


Figure 3. Polarized luminescence from MEH-PPV in aligned mesoporous silica films. The indexes refer to the pores orientation, and the excitation and emission polarizations, respectively. The polarization ratio $I_{vvv}/I_{vvh} = 12.2$, while $I_{vhh}/I_{vhv} = 0.23$.

For the polymer incorporated film, a polarization ratio of 12.2 is attained when the excitation light is parallel to the pores (I_{vvv}/I_{vvh}) (Figure 3). When the excitation light is aligned perpendicular to the pores, the ratio is 0.23 (I_{vhh}/I_{vhv}), a value that would be impossible for isolated chromophores with parallel absorption and emission dipoles.

A simple model of the expected anisotropies using the pore alignment distribution from XRD (Figure 1c) yields values close to those measured and confirms the alignment and incorporation of polymer in the pores. For absorption, the calculated value is 4.8. The emission values are 12.0 and 1.4, for excitation parallel and perpendicular to the pores, respectively. The only discrepancy is found in fluorescence with perpendicular excitation; this geometry is especially susceptible to directional energy transfer. It is reasonable that excitations on higher energy coiled or kinked chains will rapidly transfer to lower energy chains parallel to the pores within the polymer fluorescence lifetime.³ This process can efficiently lead to perpendicular fluorescence anisotropies less than 1.

Highly aligned polymers are important, but it is also advantageous if the material is densely filled. The filling fraction of the

material can be estimated by considering the absorption and film dimensions. The peak optical density of the polymer in the mesoporous film is 0.27. Absorption spectra and profilometry of varying thicknesses of spin-cast films indicates that a film with an optical density of 0.27 would be 15.3 nm thick. This comparison works because polymer chains in both the mesoporous material and the spin-cast films are dominantly aligned in the plane of the film,¹² and because polymer orientation in the plane does not affect absorption of unpolarized light. From STEM (Figure 1a), the film dimensions can be determined. In addition, BET measurements on bulk samples provide information about the amount of pore volume lost due to surface silylation.¹³ By using the average pore dimensions, the number of pores per unit area, and the film thickness, an equivalent open air thickness of 39 nm was determined for our 186 nm thick film. From the composite OD, this means that 40% of the open volume of the pores is filled with polymer. If this is correct, given the relative size of an individual pore and a polymer chain, this value would require more than one polymer chain to be incorporated in each pore.

Further, the 40% value is a lower limit. It is likely that some pores are completely inaccessible, creating unevenly distributed polymer. Thus, it stands to reason that each filled pore probably contains 2–3 chains. This could potentially lead to conducting mesochannels: in any single chain, defects prohibit conduction. However, the close proximity of other chains could give carriers a route around defect sites and allow for long-range conductivity.

Highly aligned mesoporous silica films filled with the semiconducting polymer MEH-PPV are a promising new class of host/guest structures. The polymer chains show a high degree of dipole alignment due to confinement within the silica framework. The structures have significant potential for photonic applications, as they are optically clear and emit polarized light. Additionally, they could prove useful for nanoscale electronics applications and for fundamental investigations of these polymers.

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References

- (1) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Bredas, J. L.; Salaneck, W. R. *Nature* **1999**, *397*, 121.
- (2) Breen, C. A.; Deng, T.; Breiner, T.; Thomas, E. L.; Swager, T. M. *J. Am. Chem. Soc.* **2003**, *125*, 9942.
- (3) (a) Wu, J.; Gross, A. F.; Tolbert, S. H. *J. Phys. Chem. B* **1999**, *103*, 2374. (b) Nguyen, T. Q.; Wu, J. J.; Doan, V.; Schwartz, B. J.; Tolbert, S. H. *Science* **2000**, *288*, 652.
- (4) Hagler, T. W.; Pakbaz, K.; Voss, K. G.; Heeger, A. J. *Phys. Rev. B* **1991**, *44*, 8652.
- (5) Grell, M.; Bradley, D. D. C. *Adv. Mater.* **1999**, *11*, 895 and references therein.
- (6) Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *280*, 1741.
- (7) Motamedi, F.; Ihn, K. J.; Ni, Z.; Srdanov, G.; Wudl, F. *Polymer* **1992**, *33*, 1102.
- (8) (a) Wu, C.-G.; Bein, T. *Science* **1994**, *264*, 1757. (b) Marlow, F.; McGehee, M. D.; Zhao, D. Z.; Chmelka, B. F.; Stucky, G. D. *Adv. Mater.* **1999**, *11*, 632.
- (9) (a) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710. (b) Hou, Q.; Margolese, D. I.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 1147. (c) Zhao, D. Y.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548.
- (10) (a) Tolbert, S. H.; Firouzi, A.; Stucky, G. D.; Chmelka, B. F. *Science* **1997**, *278*, 264. (b) Trau, M.; Yao, N.; Kim, E.; Xia, Y.; Whitesides, G. M.; Aksay, I. A. *Nature* **1997**, *390*, 674. (c) Kawashima, Y.; Nakagawa, M.; Ichimura, I.; Seki, T. *J. Mater. Chem.* **2004**, *14*, 328. (d) Melosh, N. A.; Davidson, P.; Feng, P.; Pine, D. J.; Chmelka, B. F. *J. Am. Chem. Soc.* **2001**, *123*, 1240.
- (11) (a) Miyata, H.; Noma, T.; Watanabe, M.; Kuroda, K. *Chem. Mater.* **2002**, *14*, 766. (b) Fukuoka, A.; Miyata, H.; Kuroda, K. *Chem. Commun.* **2003**, 284.
- (12) McBranch, D.; Campbell, I. H.; Smith, D. L.; Ferraris, J. P. *Appl. Phys. Lett.* **1995**, *66*, 1175.
- (13) Anwander, R.; Nagl, I.; Widenmeyer, M.; Engelhardt, G.; Groeger, O.; Palm, C.; Röser, T. *J. Phys. Chem. B* **2000**, *104*, 3532.

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