

Nanopatterning and Nanocharge Writing in Layer-by-Layer Quinquethiophene/Phthalocyanine Ultrathin Films

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Nanometer-scale patterning and charging in layer-by-layer (LbL) ultrathin films of quinquethiophene (5TN)/phthalocyanine (CuPS) provides a novel write–read device using a standard current-sensing atomic force microscopy (CS-AFM). The AFM height images showed dented or raised morphological features that could be selectively manipulated by changing the direction of the bias voltages. The conductivity was repeatedly changed between a conductive and insulating state, originating from an electrochemical charging–discharging effect. This was attributed to electrochemical ion transport and the residual mobile ions present in LbL films. Finally, the nanocharge pattern was written by CS-AFM and read out in a conductivity map image.

The manipulation of electrically conductive and semiconductive surface properties has been of considerable interest in nanometer-scale electronic devices such as data storage, memory devices, and nanosensors. Various techniques of nanostructuring have been reported using atomic force microscopy (AFM), which include electrical nanolithography to fabricate a charged dielectric surface,¹ electrostatic nanolithography,² dip-pen nanolithography,³ and electrochemical nanopatterning.⁴ These techniques have been applied to fabricate conjugated polymer nanopatterns by direct electropolymerization⁵ and by the electrochemical conversion of an insulating precursor polymer to a conducting polymer via cross-linking.^{6,7} To our knowledge, only a few groups have explored nanostructures using organic semiconductor films for memory-data storage. Yang and co-workers reported nonvolatile organic film memory devices, which used the electric-field-induced charge-transfer property between gold nanoparticles and 8-hydroxyquinoline.⁸ However, the protocol for write–read nanostructures has not been adequately reported.

In this work, we report the manipulation of nanometer-scale write–read organic semiconductor layer-by-layer (LbL)⁹ ultrathin film devices using electrochemical AFM nanolithography. Since π -conjugated and semiconductor organic films can be positively charged by anion doping, negatively charged by cation doping, and discharged by dedoping, in principle, these films can be repeatedly switched between conducting and insulating states. Thus, it should be possible to fabricate a write–read–erasable memory device. To investigate the possibility of nanometer-scale charging, we have utilized quinquethiophene (5TN)/phthalocyanine (CuPS) films prepared using the LbL deposition technique. The LbL self-assembly method, initially reported by Decher et al., is one of most convenient techniques for fabricating molecularly controlled ultrathin multilayer films.¹⁰ The adsorption process involves alternate electrostatic deposition of cationic and anionic species from solution.¹¹ A number of groups have reported the LbL deposition of conducting organic and polymer materials.¹² Recently, we reported the

LbL deposition of bolaamphiphile oligothiophenes and found that aggregation in solution can be used to tune the amount of surface coverage in ultrathin films.¹³

Figure 1 shows the strategy for fabricating a nanometer-scale write–read memory device and the chemical structures of the materials used in this study. First, an LbL film of a positively charged bolaamphiphilic quinquethiophene (5TN) and negatively charged phthalocyanine-3,4',4'',4'''-tetrasulfonic acid, tetrasodium salt (CuPS) was deposited on a gold-coated substrate. Then, the film was nanolithographically charged or discharged by applying appropriate voltages using the current-sensing AFM (CS-AFM) technique. For simplicity of discussion, a positive electric field is defined when the Au surface is positively biased, and a negative electric field is defined when the Au surface is negatively biased. Since 5TN and CuPS are conjugated oligomeric organic materials and mobile ions can be incorporated in the LbL films during deposition process,¹⁴ 5TN/CuPS LbL films are expected to be charged (doped) in ambient air without any added electrolyte. We have preliminarily shown that the 5TN/CuPS LbL films could be charged in indium tin oxide (ITO)/5TN–CuPS/Al devices, and this was confirmed to be due to an electrochemical charging effect. This is because the electrochromic effect was observed at the same time.¹⁵ Heeger and co-workers reported that conjugated polymers could be charged as both n-type and p-type in a solid-state electrochemical cell.¹⁶ This enabled changing the conducting–insulating state of conjugated films in the solid state after the fabrication of the device, and they applied this property to light-emitting electrochemical cells and polymer field-effect transistors (FETs). In addition to the electrochemical effect in a solid-state cell, humidity or water meniscus around the cantilever/sample surface could facilitate the electrochemical effect in the case of AFM nanolithography in ambient air.¹⁷

To begin with, we utilized bolaamphiphilic 5TN, which contains quaternary ammonium endgroups, and CuPS as the organic cation and anion, respectively, for the LbL ultrathin film assemblies. The details of the synthesis procedure for the 5TN has been described in a previous publication.¹³ The

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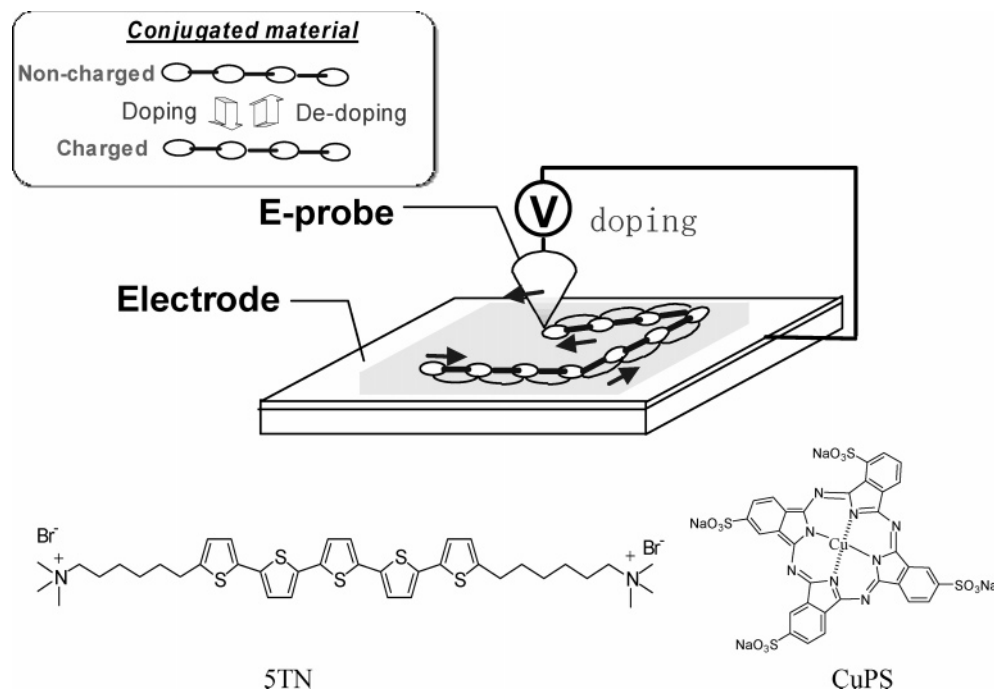


Figure 1. Schematic illustration of the fabrication of a nanometer-scale write–read memory device and the chemical structures used in this study.

electrostatic LbL adsorption was performed following the Decher approach.¹⁰ The gold surface of the flat solid substrate was functionalized by immersing the slide for 1 h in an ethanol solution of 3-mercapto-1-propanesulfonic sodium salt (1mM) (followed by rinsing), creating a uniformly charged (negative) substrate surface. The gold film with a thickness of ~ 50 nm, was deposited by vacuum evaporation onto a BK7 glass slide with a 1–2 nm thick chromium adhesion layer. The Au/Cr/glass substrates with the functionalized surfaces were alternately immersed for 15 min in aqueous solutions of the cation and anion until the desired layer number was achieved. Rinsing with deionized water at pH 5.6 (Milli-Q, 18 M Ω) was performed between depositions. Aqueous solutions of the 5TN and CuPS were prepared with a concentration of 1 mg/ml. All writing experiments were done with a commercial CS-AFM (PicoScan system or PicoPlus system, Molecular Imaging, Arizona) and Pt-coated cantilever. All patterning experiments were conducted under ambient conditions at $\sim 50\%$ relative humidity and 22 °C. Subsequent images after patterning were performed under same conditions.

The evaporated gold film (~ 50 nm) on BK7 glass/Cr was used as the bottom electrode. The Pt-coated cantilever was brought into contact (~ 0.5 nN) with the LbL film surface under ambient conditions. Figure 2 shows the AFM height images after applying a positive and negative bias at a scan rate of 1 μ m/sec in which the thickness changed after writing. The raised and dented features are selectively observed when a positive and negative bias is applied, respectively. The thickness change is also shown in the figure. As Lyukusyutov and co-workers have shown with poly(methyl methacrylate) (PMMA) films, these selective features could be explained by electrostatic joule-heating lithography.² Besides the joule-heating effect, since the ion mobility is greatly enhanced in solid-state cells when the temperature exceeds T_g or T_m ,¹⁶ the joule heating could facilitate the ion transport in the film. In fact, Wee and co-workers showed that the features of PMMA films can be changed by ion transfer due to joule heating.¹⁸ Thus, the reason for the selective change of morphology may be attributed to both electrostatic joule heating and the ion-mobility effect, which contributes to mass

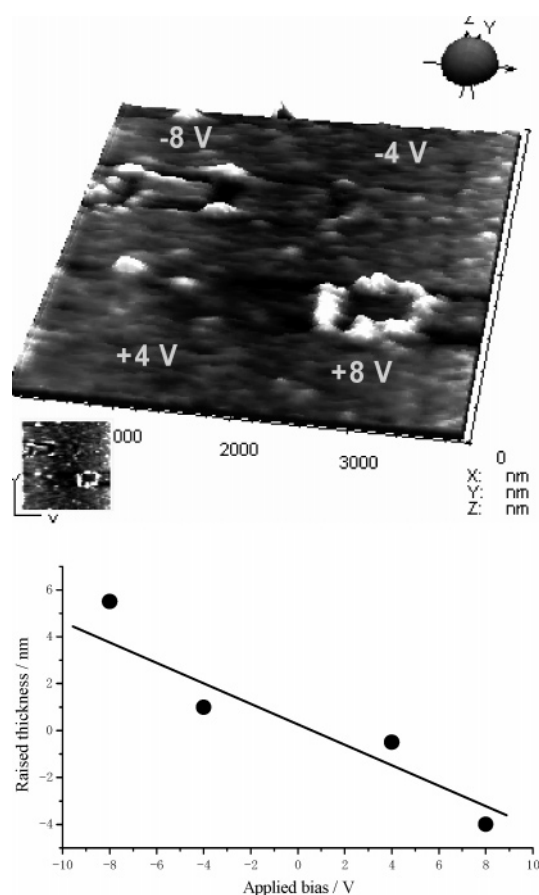


Figure 2. AFM height images of 5TN/CuPS LbL film (4 bilayers) after writing at positive and negative bias, respectively, and the thickness changed after writing.

transport. On the basis of our finding that the electrochemical charging effect can be obtained when applying voltage to an ITO/STN—CuPS/Al sandwich structure in ambient air,¹⁵ a charging/doping effect is expected in addition to just ion transport in the film. It is well-known that conjugated polymer

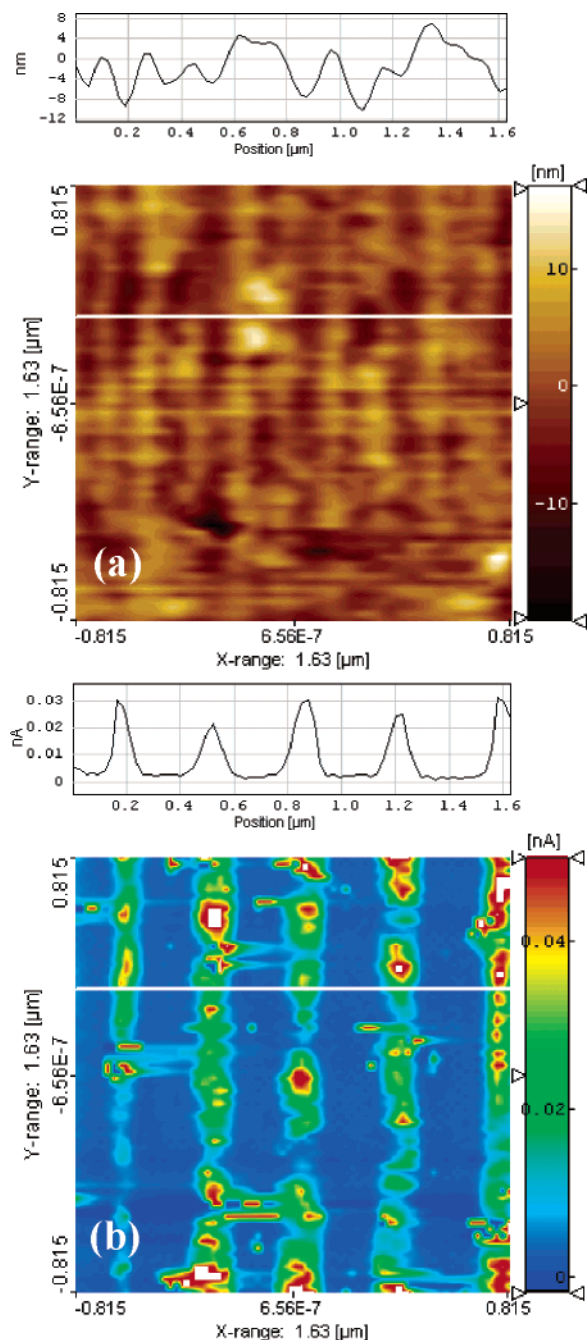


Figure 3. Morphology (a) and conductivity map (b) of 5TN/CuPS LbL film (10 bilayers) scanned at +1 V after writing the lines at +5 V.

films are electrochemically charged when the applied voltage exceeds the band gap energy. This phenomenon corresponds to our experiments done with the CS-AFM. The changes observed in the experiments were observed at energies higher than the energy band gap (E_g) of both 5TN ($E_g \approx 2.3$ eV) and CuPS ($E_g \approx 3.0$ eV). Since the 5TN/CuPS film is a p-type material, it is expected that the p-type doping (transfer of anion) is dominantly generated, while a small amount of cation transfer is expected. Anions from both the water meniscus and the residual ions inside the film move to the Au surface when applying a positive bias, whereas only anions from residual ions are attributed to ion transport inside the film when applying a negative bias.

To investigate the electrochemical charging/doping effect in this system, topographical morphology and current images were simultaneously observed. For the patterning, voltages were

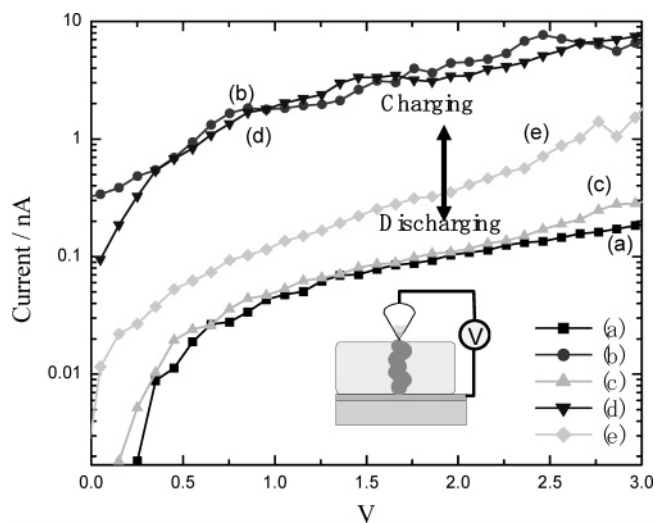


Figure 4. I–V properties of the Au/5TN–CuPS/Pt-coated cantilever system before and after charging. (a) Before charging, (b) after charging at +8 V for 10 s, (c) after discharging at 0 V for 10 s, (d) after charging at –8 V, and (e) after discharging at 0 V for 10 s. These measurements and charging/discharging were continuously carried out from a–e.

applied for 100 nm for each line (5 lines in $2 \times 2 \mu\text{m}$ scale) at +5 V while scanning at a scan rate of $290 \mu\text{m}/\text{sec}$. It should be noted that +5 V does not give significant patterned features,¹⁵ even though it is higher than the band gap energies of 5TN and CuPS. Figure 3 shows the topographical height image (panel a) and current image (panel b) scanned at 1 V after patterning. With the lines in height image, no obvious pattern was observed; however, clear nanolines were observed in the current image. The current image shows that these lines are more conductive and the charges are retained, as can be read out after writing. The fact that the conductivities are increased after applying the bias confirms that an electrochemical ion transfer-charging effect is observed; that is, the mechanism of morphological changes observed is not only due to the joule heating. The current in each line is in the range of 30–50 pA which is 10 times higher than the blue area. This result clearly shows that the charged patterns can be created by CS-AFM nanolithography.

Figure 4 shows the current–voltage (I–V) properties in the system of Au/5TN–CuPS/Pt-coated cantilever before charging (panel a), after charging at +8 V (panel b), after discharging at 0 V (short circuit; panel c), after charging at –8 V (panel d), and after discharging at 0 V (panel e). These measurements and charging/discharging were continuously carried out from a–e while scanning one line. This indicates that the 5TN/CuPS films can be repeatedly switched between high- and low-conductivity states by reversibly applying voltages. The films at first have low conductivity (discharged state), which is changed to a higher-conductive (charged) state by applying both positive and negative biases. The higher-conductive state was erased by applying 0 V (short circuit) during scanning. This write–read–erase cycle demonstrates that the device can be used as a memory device. The I–V property after discharging (after charging at +8 V) still retained a small conductive state, although this was completely erased when applying 0 V for more than 20 s. This is probably because the additional ions from the water meniscus are hardly removed from the film when applying 0 V, which does not have the assistance of joule heating. From the I–V curve properties, the conductivity is roughly estimated to be in the range of 10^{-3} – $10^{-4} \text{ S}\cdot\text{cm}^{-1}$ after charging, and 10^{-5} – $10^{-6} \text{ S}\cdot\text{cm}^{-1}$ after discharging.

In summary, we demonstrated the nanometer-scale charging in conjugated LbL ultrathin films, which provides a novel

write—read device using a standard CS-AFM. The AFM height images showed dented features or raised features that could be selectively manipulated by changing the direction of the bias voltages. The charged patterns were obtained after applying a minimum voltage, while morphological change was not necessarily observed. This was attributed to the electrochemical ion transport and charging, which was assisted by the water meniscus (tip/cantilever—substrate) and joule heating. The conductivity was repeatedly changed between a conductive and insulating state, originating from an electrochemical charging—discharging effect. Compared with other approaches that have been demonstrated to be effective in creating a charge storage device using ferroelectric materials, our method utilizes organic semiconductor ultrathin films that can be charged/discharged by low voltages via the electrochemical doping effect. The demonstrated method should provide new opportunities for both basic studies of nanocharging patterns and nanoscale electronic device applications using other organic semiconductor materials. Further studies are underway to relate film thickness, controlled humidity, and other LbL combinations of different organic semiconductor materials.

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Supporting Information Available: Cyclic voltammogram of 5TN/CuPS LbL films in aqueous solution, electrochemical effect in the Al/LbL/ITO sandwich structure, and AFM and LFM read—write—erase experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

(1) Mesquida, P.; Knapp, H. F.; Stemmer, A. *Surf. Interface Anal.* **2002**, 33, 159.

- (2) Lyuksyutov, S. F.; Vaia, R. A.; Paramonov, P. B.; Juhl, S.; Waterhouse, L.; Ralich, R. M.; Sigalov, G.; Sancaktar, E. *Nat. Mater.* **2003**, 2, 468. (b) Lyuksyutov, S. F.; Paramonov, P. B.; Juhl, S.; Vaia, R. A. *Appl. Phys. Lett.* **2003**, 83, 4405. (c) Juhl, S.; Phillips, D.; Vaia, R. A.; Lyuksyutov, S. F.; Paramonov, P. B. *Appl. Phys. Lett.* **2004**, 85, 1.
- (3) Piner, R. D.; Zhu, J.; Xu, F.; Hong, S. H.; Mirkin, C. A. *Science* **1999**, 283, 661. (b) Hong, S. H.; Zhu, J.; Mirkin, C. A. *Science* **1999**, 286, 523.
- (4) Schneegans, O.; Moradpour, A.; Houze, F.; Angelova, A.; Ville-neuve, C. H.; Allongue, P.; Chretien, P. *J. Am. Chem. Soc.* **2001**, 123, 11486.
- (5) Maynor, W.; Filocamo, S. F.; Grinstaff, M. W.; Liu, J. *J. Am. Chem. Soc.* **2002**, 124, 522.
- (6) Jang, S.-Y.; Mearquez, M.; Sotzing, G. A. *J. Am. Chem. Soc.* **2004**, 126, 9476.
- (7) Jegadesan, S.; Advincula, R. C.; Valiyaveetil, S. *Adv. Mater.* **2005**, 17, 1282.
- (8) Ouyang, J.; Chu, C.-W.; Szmada, C.; Ma, L.; Yang, Y. *Nat. Mater.* **2004**, 3, 918.
- (9) Advincula, R.; Locklin, J.; Youk, J.; Xia, C.; Park, M.-K.; Fan, X. *Langmuir* **2001**, 18, 877.
- (10) Decher, G.; Hong, J. D. *Makromol. Chem., Macromol. Symp.* **1991**, 46, 321.
- (11) Baba, A.; Kaneko, F.; Advincula, R. C. *Colloids Surf., A* **2000**, 173, 39.
- (12) Baba, A.; Park, M.-K.; Advincula, R. C.; Knoll, W. *Langmuir* **2002**, 18, 4648. (b) Cheung, J. H.; Fou, A. F.; Rubner, M. F. *Thin Solid Films* **1994**, 244, 985. (c) Zhai, L.; McCullough, R. D. *Adv. Mater.* **2002**, 14, 901. (d) Park, M.-K.; Onishi, K.; Locklin, J.; Caruso, F.; Advincula, R. C. *Langmuir* **2003**, 19, 8550.
- (13) Locklin, J.; Youk, J. H.; Xia, C.; Park, M.-K.; Fan, X.; Advincula, R. C. *Langmuir* **2002**, 18, 877. (b) Xia, C.; Locklin, J.; Youk, J. H.; Fulghum, T.; Advincula, R. C. *Langmuir* **2002**, 18, 955.
- (14) Durstock, M. F.; Rubner, M. F. *Langmuir* **2001**, 17, 7865. (b) Locklin, J.; Shinbo, K.; Onishi, K.; Kaneko, F.; Bao, Z.; Advincula, R. C. *Chem. Mater.* **2003**, 15, 1404. (c) Schmitt, J.; Grunewald, T.; Decher, G.; Pershan, P. S.; Kjaer, K.; Losche, M. *Macromolecules* **1993**, 26, 7058. (d) Schlenoff, J. B.; Li, M. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, 100, 943. (e) Shinbo, K.; Suzuki, K.; Kato, K.; Kaneko, F.; Kobayashi, S. *Thin Solid Films* **1998**, 327, 209.
- (15) See Supporting Information.
- (16) Pei, Q.; Yu, G.; Chang, C.; Yang, Y.; Heeger, A. J. *Science* **1995**, 265, 1086. (b) Edman, L.; Swensen, J.; Moses, D.; Heeger, A. J. *Appl. Phys. Lett.* **2004**, 84, 3744. (c) Edman, L.; Summers, M. A.; Buratto, S. K.; Heeger, A. J. *Phys. Rev. B* **2004**, 70, 115212.
- (17) Schneegans, O.; Moradpour, A.; Boyer, L.; Ballutaud, D. *J. Phys. Chem. B*, **2004**, 108, 9882.
- (18) Xie, X. N.; Chung, H. J.; Sow, C. H.; Bettiol, A. A.; Wee, A. T. *S. Adv. Mater.* **2005**, 17, 1386.