

Electronic Supplementary Information

Writing Nanopatterns with Electrochemical Oxidation on Redox Responsive Organometallic Multilayers by AFM

Jing Song,^{1,2} Mark A. Hempenius, Hong Jing Chung,^{2,3} G. Julius Vancso^{2*}

¹*Institute of Materials Research and Engineering, Research Link 3, 117602, Singapore.*

²*Materials Science and Technology of Polymers, MESA⁺ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands.*

³*Data Storage Institute, 5 Engineering Drive 1, Singapore, 117608*

Corresponding Author E-mail: g.j.vancso@utwente.nl

Experimental

Materials

Positively and negatively charged polyferrocenylsilanes (PFS)s (weight average molar mass $M_w = 5.3 \times 10^4$ g/mol with a PDI = 1.3) were synthesized by catalytic ring opening polymerization (ROP) of stranded chlorinated cycloferrocenophane, followed by the modification of the side group as described previously.¹ All other reagents, 3-aminopropyltrimethoxysilane, hydrogen peroxide solution 30 % (w/w), ammonium hydroxide solution 28% (w/w), sodium perchlorate (NaClO₄) were purchased from Sigma-Aldrich and used without further purification. Solvents (toluene, ethanol) were of analytical grade and used to make the solutions and rinse the substrates.

PFS Multilayer fabrication

Multilayers were deposited on indium tin oxide (ITO)-glass (Ssens, Hengelo, the Netherlands), which were cleaned prior to use. The cleaning procedure was as follows: the substrate was immersed into a mixture of H₂O, H₂O₂ and NH₄OH with a volume ratio of 5:1:1 for 20 min, and

then the substrate was rinsed extensively with Milli-Q water and dried under a nitrogen stream. The clean ITO substrates were immersed in a toluene solution of 3-aminopropyltrimethoxysilane (0.1 mM) to impart positive charges onto the substrates. The modified substrates were alternatively immersed into aqueous solutions of the polycation (PFS⁺) and polyanion (PFS⁻) (2 mg/ml of polymer and 0.5 M NaCl) for 10 minutes. The substrates were rinsed between steps by being immersed in pure Milli-Q water and being subsequently dried with a stream of nitrogen gas.

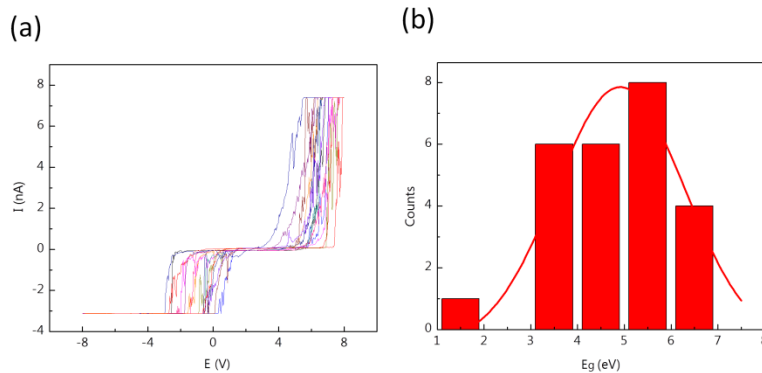
EDPN experiments on PFS multilayers

Contact mode AFM was used to carry out EDPN experiments using a Dimension 3100 SPM (Bruker-Digital Instruments, Santa Barbara, CA) with a NanoScope IV controller and Nanoman software. For electrochemical writing Pt/Cr coated silicon probes (Nanosensors, Wetzlar, Germany, with a spring constant of 0.2N/m) were immersed in electrolyte solutions (0.1M NaClO₄) for 5 min. The patterns were written in the contact mode and with the application of a DC voltage under a preset load force of about 0.1nN. Selected values of tip voltage or sample bias were applied and relative humidity was recorded. The PFS multilayers assembled on ITO substrates were grounded with silver paste during all measurements. The topographic height and width values reported here were obtained by analyzing 5 height and 5 width line profiles, respectively. As a comparison, EDPN experiments were carried out with a Dimension ICON (Bruker, Germany) equipped with an extended, tunneling AFM (TUNA) module in the tapping mode. Pt/Cr coated silicon probes (Nanosensors, Wetzlar, Germany, with a spring constant of 40N/m) were used. Following electrochemical DPN, tapping mode imaging with a freshly cleaned silicon probe on the patterned area was performed. In order to measure the current flow through the AFM conductive tip while applying a voltage between the tip and the substrate, a

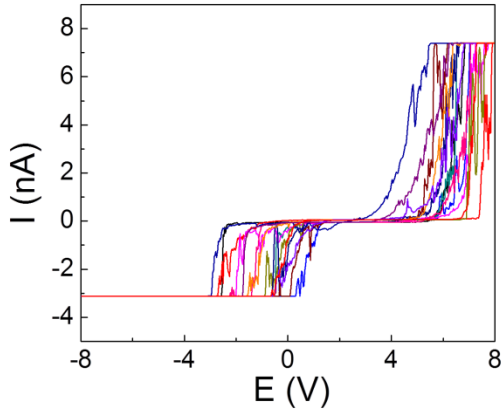
tunneling AFM (TUNA) module was used to characterize the electrical properties of the multilayer thin film with high sensitivity ($<1\text{pA V}^{-1}$). I/V measurements were recorded with forward and reverse tip bias scans between -8V and 8V .

Electronic properties of PFS multilayers with conducting AFM

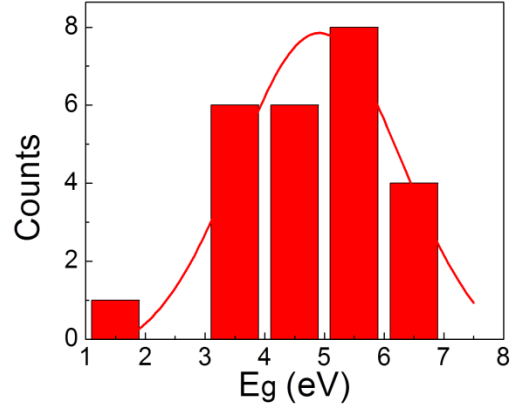
We describe some current/potential characteristics we obtained by AFM in the tunneling TUNA mode. Here we focused on determining band gap energy values as the AFM Tuna mode allows one to obtain such characteristics. It is possible to assign the band gap energy value for I/V curves obtained by C-AFM by measuring the distance between the first two points showing response.^{2,3} Figure E1a depicts a total of 20 I/V curves for PFS₅ bilayer measured by AFM in the TUNA mode. The obtained band gap E_g values ranged from 1.75 to 6.87 eV depending on the spot analyzed from point to point. The histogram of band gap value distribution is shown in Figure 6b. This result is useful as it indicates a semiconducting response of the PFS. However, the band gap values obtained cannot be considered as to represent the intrinsic electrical characteristics of the PFS used due to the experimental method and data variation with the choice of the spot and measurement conditions.



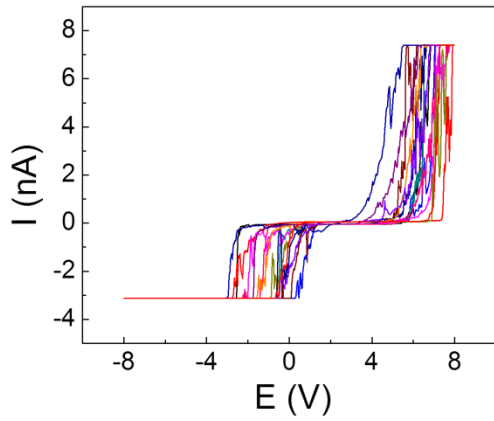
(a)



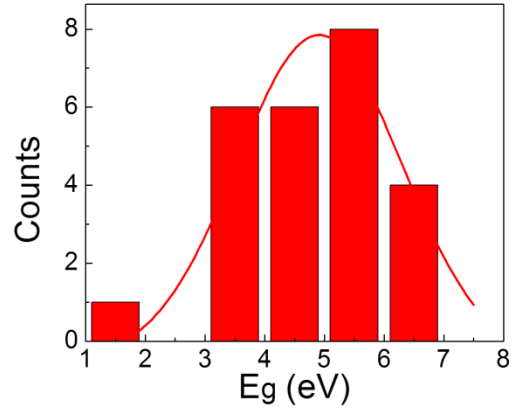
(b)



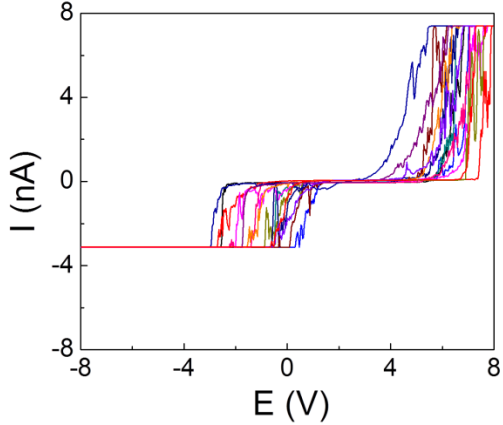
(a)



(b)



(a)



(b)

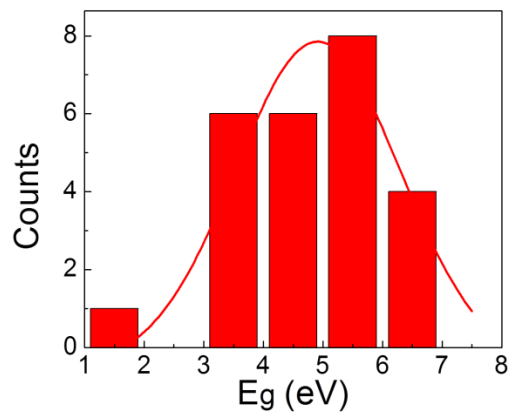


Figure E1 (a) Typical current voltage (I/V) curves (0.1 nA/div amplifier) on a PFS₅ thin film in a scan range of -8V to +8V. (b) Histogram of the bandgap E_g value distribution. The average E_g value is 4.9 eV.

ESI Reference List

1. M. A. Hempenius, F. F. Brito and G. J. Vancso, *Macromolecules*, 2003, **36**, 6683-6688.
2. B. Alperson, S. Cohen, I. Rubinstein and G. Hodes, *Phys. Rev. B*, 1995, **52**, 17017-17020.
3. B. Alperson, I. Rubinstein and G. Hodes, *Phys. Rev. B*, 2001, **63**, 081303(R).