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Supporting Information

A Multilevel Memory from a Multi-redox Polyoxometalate Hybrid Polymer

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Contents

Instrumentation

^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were measured at 300 MHz on a Bruker 400 AVANCE Ⅲ spectrometer with dimethyl sulfoxide-d_6 (DMSO-d_6) as the solvent. Fourier transform infrared (FT-IR) spectra were obtained with a Perkin ElmerFrontier spectrometer. Uv-Vis absorption spectra were recorded on a Shimadzu 2501 PC spectrophotometer at room temperature. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 instrument under a nitrogen atmosphere with the gas-flow rate of 50 mL/min and a heating rate of 10 C/min. Differential scanning calorimetry (DSC) measurements were carried out on a TA Instruments TA DSC Q10 system under a nitrogen atmosphere with a gas-flow rate of 50 mL/min and a heating rate of 20 °C/min. Glass transition temperature was recorded as the temperature at the middle of the thermal transition in the second heating scan. Gel permeation chromatography (GPC) traces of the samples were monitored on a an Agilent 1260 GPC - MDS system fitted with differential refractive index (DRI) and Ultraviolet (UV) detectors using THF as the eluent and linear polystyrenes as the molecular weight standards. Cyclic voltammetry (CV) measurements were carried out with a CHI 604E Electrochemical Workstation (CH Instruments, Shanghai Chenhua Instrument Corporation, China) under an argon atmosphere. The polymer film coated on a Pt electrode (working electrode) was scanned at 1 mV/s in a 0.1 M solution of tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) in acetonitrile, with a Pt wire and platinum gauze as the reference and counter electrodes, respectively. The thickness of the hybrid polymer film was measured by a KLA Tencor Alpha-Step Surface Profiler. The *I*-*V* characteristics were measured at room temperature by Keithley 4200 SCS semiconductor characterization system with voltage sweeping mode. During the measurement, a bias voltage was applied between the top and bottom (ITO) electrodes with the latter being grounded, unless otherwise specified.

Reagents for synthesis

Anderson-type polyoxomolybdates $[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3\text{-}CNH_2\}_2]$were synthesized and purified according to the reported method.[1]All other reagents and solvents were of analytical grade and used without further purification.

Synthesis of the POM monomer (MAPOM)

The synthetic process is revised from the reported method.[2]To a 100 mL schlenk bottle is added 1.8221 (1mmol) $[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3\text{-}CNH_2\}_2]$, 1.49 mL (10 mmol) of methacrylic anhydride and 20 mL acetonitrile. The reaction mixture is stirred at 50 ^{o}C under argon overnight. After cooled to room temperature, the obtained mixture was filtered, and the filtration was exposed to ether vapor diffusion. Red stick crystals are obtained after about one week. The crystals are washed with ether and dried for two days under vacuum. Yield is 91.6%. ^{1}H NMR (d_6-DMSO, 300MHz, ppm): 0.94 (36H, $–CH_3$ from TBA^+), 1.31 (24H, $–CH_2$ from TBA^+), 1.57 (24H, $–CH_2$ from TBA^+), 3.16 (24H, $–CH_2$ from TBA^+), 3.31 (6H, s, $-CH_3$), 5.08 (2H, s, vinyl), 5.44 (2H, s, vinyl), 7.10(2H, br, NH), 64.00 (12H, br, $–CH_2$). FT-IR (cm^{-1}, KBr): 3468 (br, m), 2962 (m), 2874 (m), 1670 (m), 1482 (m), 941 (s), 920 (s), 665 (vs).

Synthesis of the POM hybrid polymer (PMMA-MAPOM)

The copolymerization procedure can be revised from the reported methods.[3,4]In a typical polymerization procedure, a 100 mL schlenk bottle was charged with MMA (4.0048g, 40 mmol), MAPOM (0.2018 g, 0.1 mmol), ABCN (0.0521g, 0.2 mmol) and acetonitrile (15 mL) and heated at 90 ^{o}C under argon for 24 h. Precipitation by the addition of methanol yielded the polymers as white powders, which were filtered and washed thoroughly with methanol to remove the starting material MMA.The^{1}H NMR spectra of PMMA-MAPOM is shown in Figure S4. FT-IR(cm^{-1}, KBr): 2999 (w), 2953 (w), 1732 (s), 1482 (m), 1146 (s), 990 (m), 742 (m), 670 (m).

Fabrication and characterization of memory devices

The ITO glass substrates were pre-cleaned with ethanol, acetone and isopropanol sequentially in an ultrasonic bath for 15 min. A 0.1mL cyclohexanone solution of PMMA-MAPOM (1.0 wt % polymer) was spin-coated onto the substrates at a spinning speed of 400 rpm for 12s and then4000 rpm for 40s, followed by a vacuum-drying at 80°C for 8 h. Before spin-coating, the solution was filtered through polytetrafluoroethylene (PTFE) membrane micro-filters with a pore size of 0.45 μm. The thickness of the polymer films are about 70 nm as measured by a KLA Tencor Alpha-Step Surface Profiler. To construct the ITO/polymer/Pt structures, Pt top electrodes with a diameter of 100 μm and thickness of 300 nm were deposited at room temperature by E-beam evaporation with a metal shadow mask. The current–voltage (*I–V*) characteristics of the ITO/polymer/Pt devices were measured in an ambient atmosphere on Keithley 4200 SCS semiconductor characterization system in voltage sweeping mode. The sweeping step is 0.01 V.

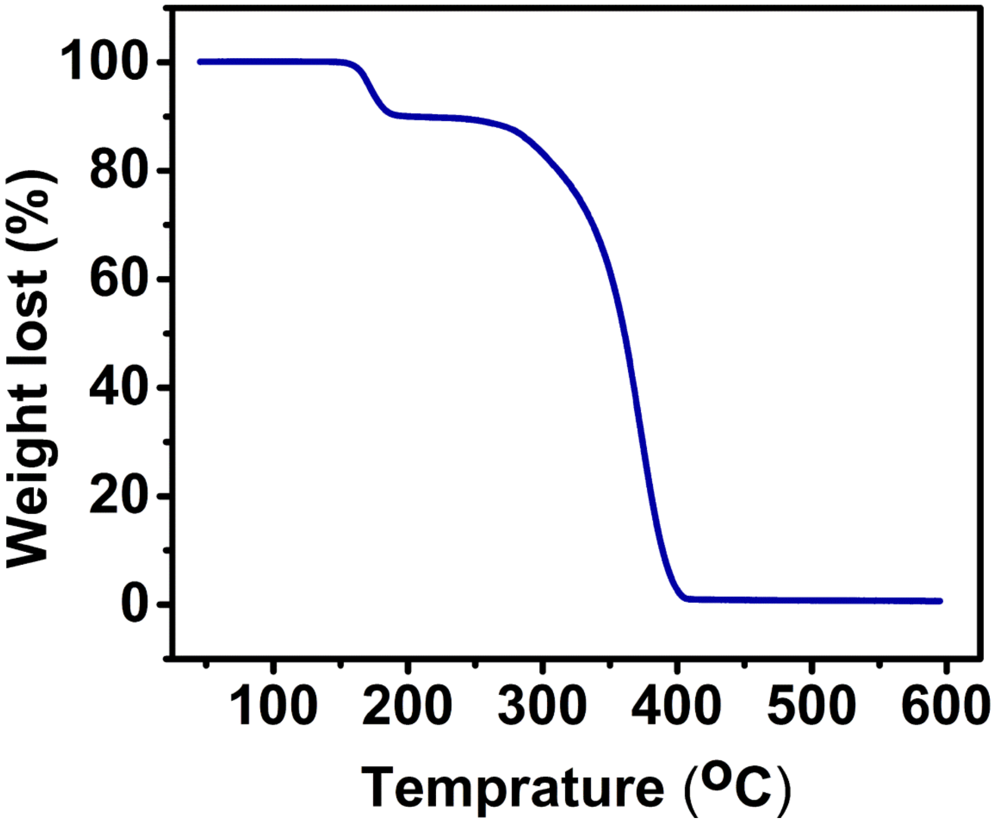

Figure S1. TGA curve of PMMA-MAPOM under an argon atmosphere at a heating rate of 10 °C min^{-1}.

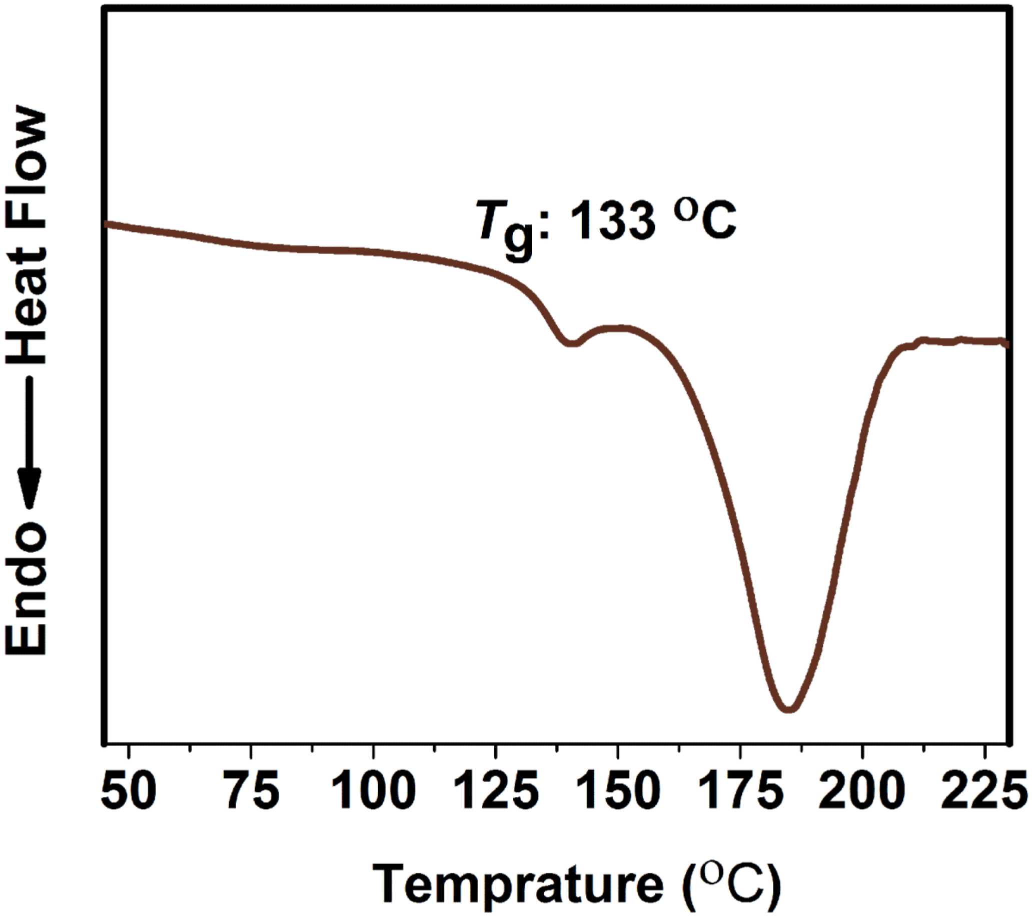

Figure S2. DSC curve of PMMA-MAPOM under an argon atmosphere at a heating rate of 20 °C min^{-1}.

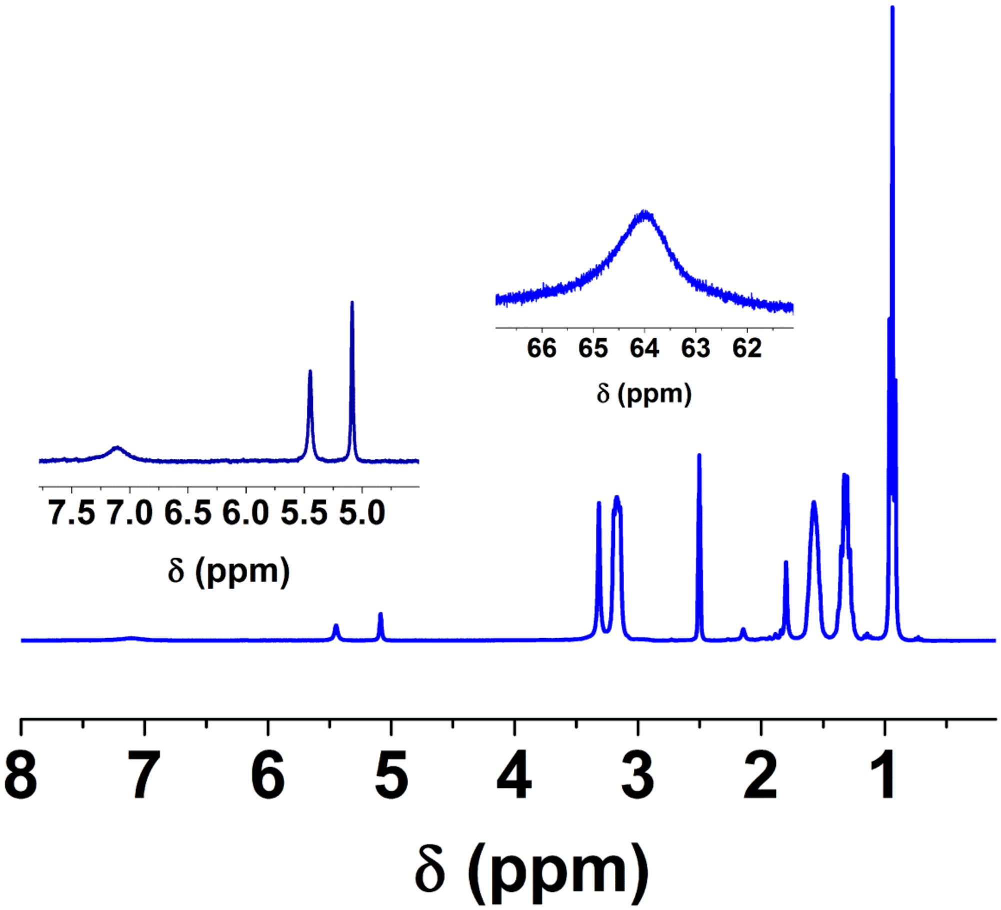

Figure S3. ^{1}H NMR spectra of MAPOM in DMSO-d_6.

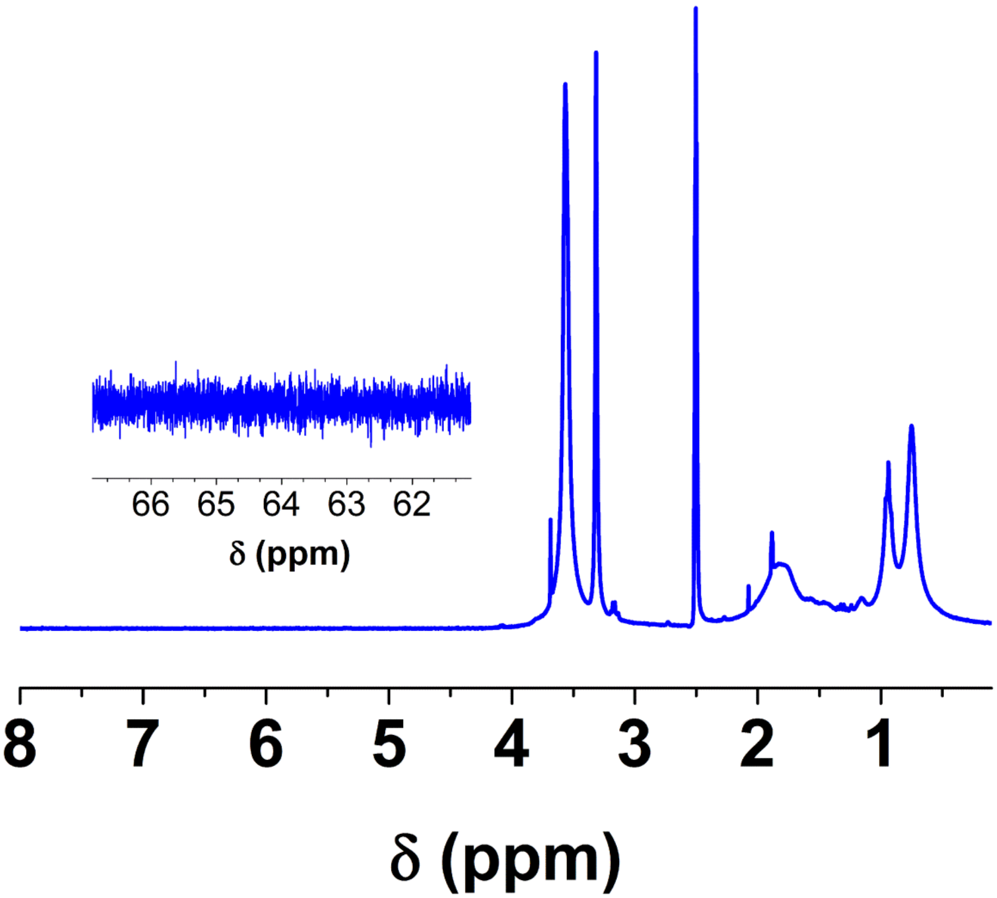

Figure S4.^{1}H NMR spectra of PMMA-MAPOM in DMSO-d_6

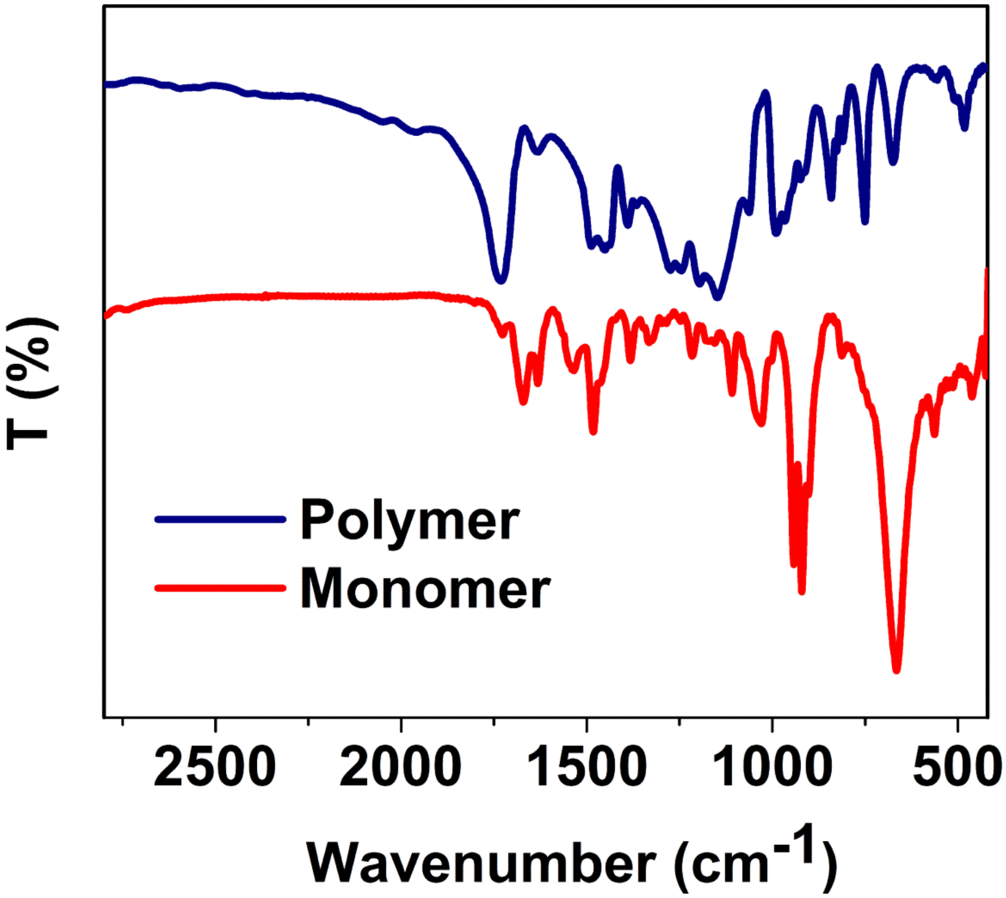

Figure S5. The FT-IR of MAPOM and PMMA-MAPOM

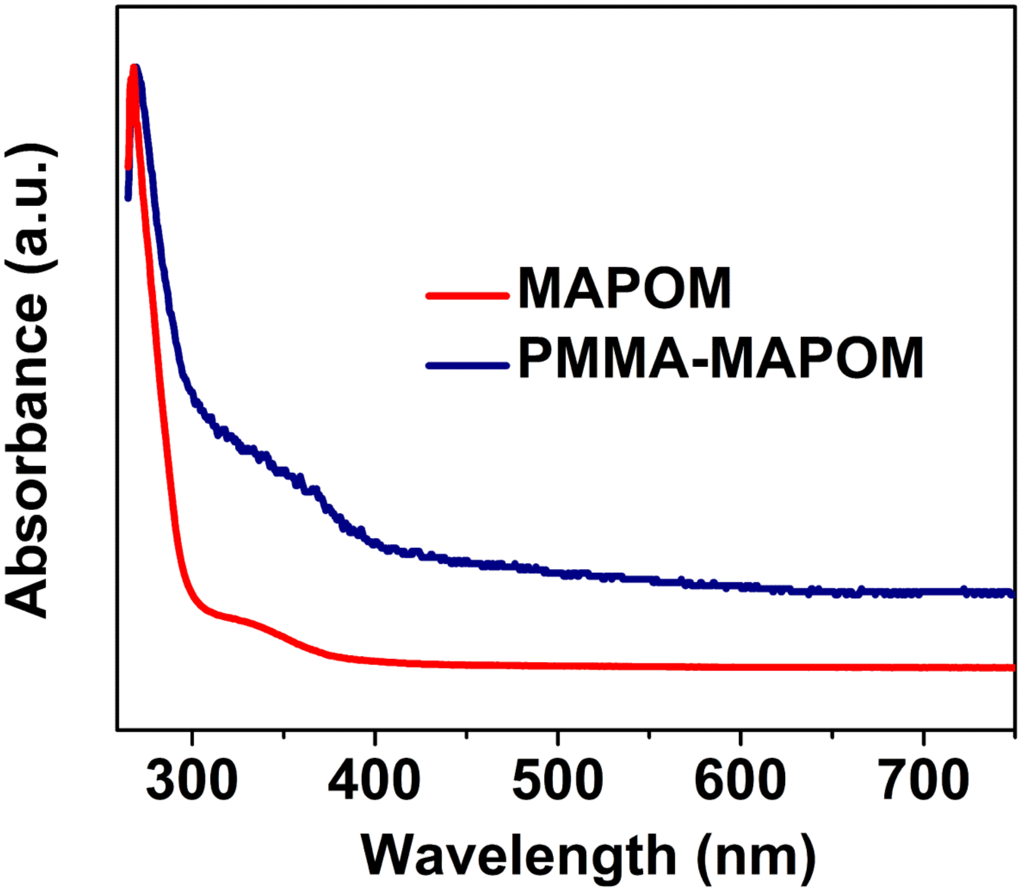

Figure S6. The UV-Vis spectra of MAPOM and PMMA-MAPOM

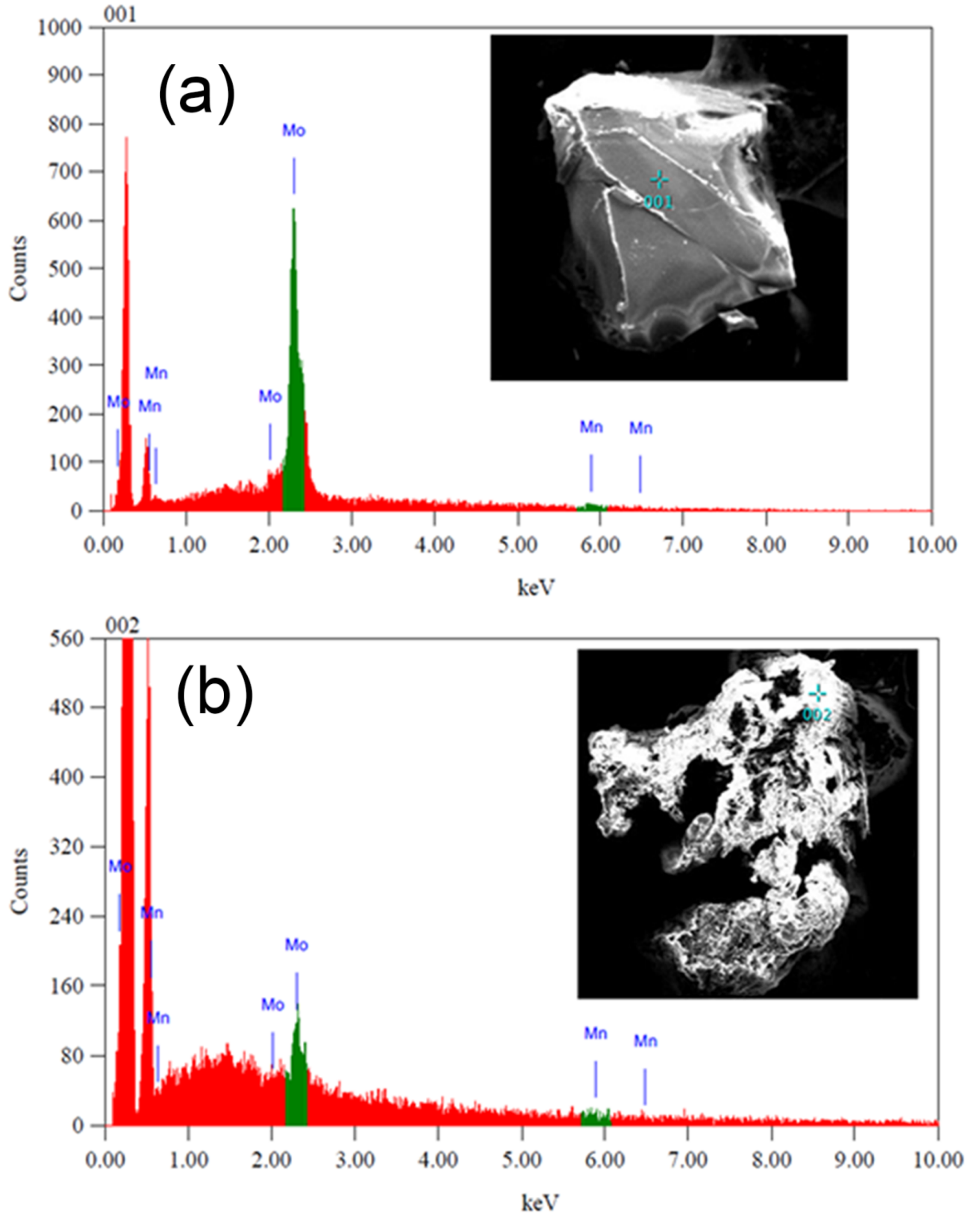

Figure S7. The EDX of MAPOM (a) and PMMA-MAPOM (b).

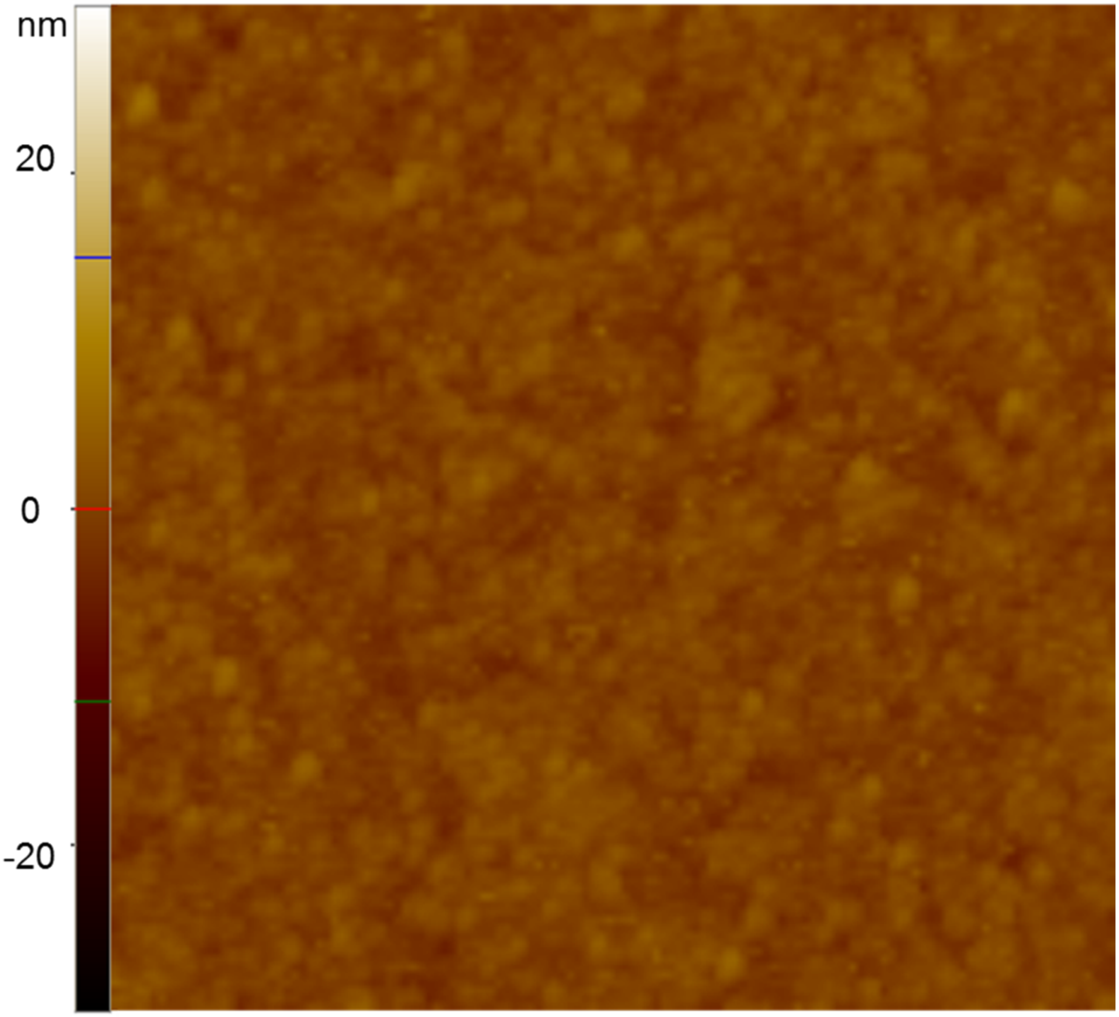

Figure S8. The AFM image of PMMA-MAPOM film on ITO glass. The scan area is 4 *μ*m × 4 *μ*m.

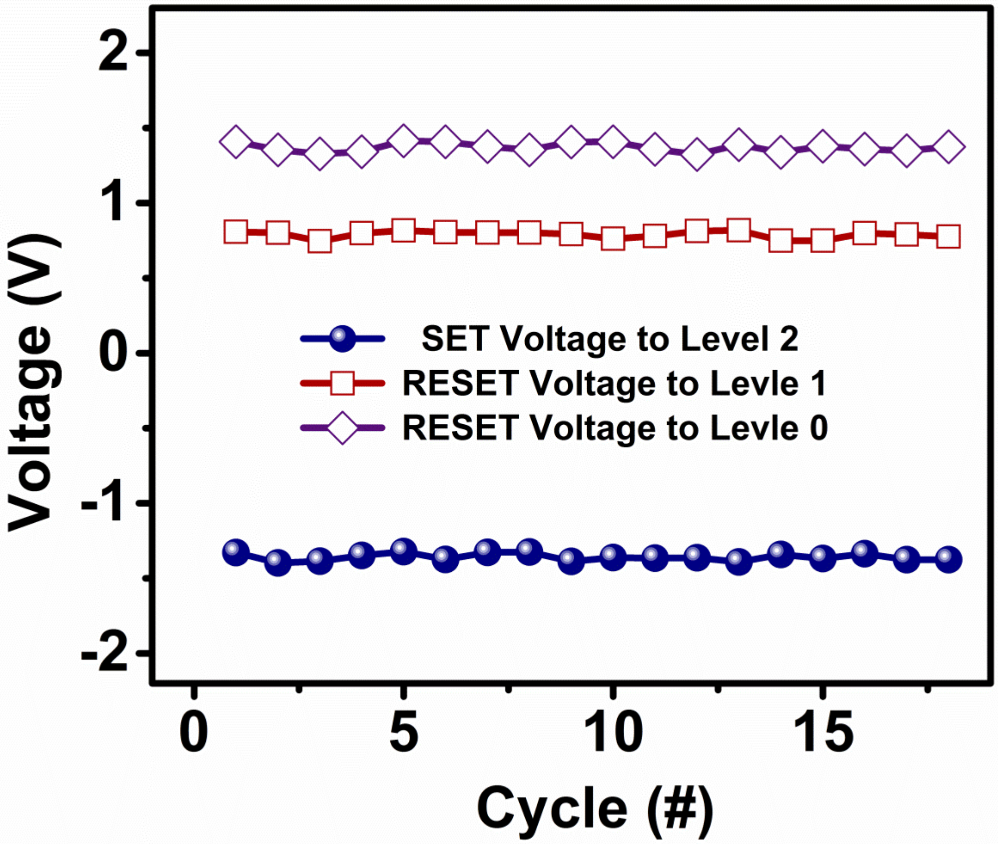

Figure S9. The distribution of operation voltages of the ITO/PMMA-MAPOM/Pt device

References

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