Supporting Information

Micropatterning of Conducting Polymer Thin Films on Reactive Self-Assembled Monolayers

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Synthesis of Compound 1: A mixture of 1,4-di-iodo-2,5-hydroquinone (1.9g, 5.25 mmol), 6-(Boc-amino)-1-bromo-hexane (4g, 15 mmol), KOH (0.89g, 15.8 mmol), and DMSO (20 ml) was stirred at room temperature for 24 h and then poured into water. The solid precipitate out and was purified by chromatography (silica gel, dichloromethane/hexane (2/1)) (3.2 g, 83%). *^{1}H NMR* ($CDCl_3$, ppm): 1.40-1.45 (m, 22H, $-CH_3$, $-CH_2-$), 1.53 (m, 4H, $-CH_2-$), 1.85 (m, 4H, $-CH_2-$), 3.17 (m, 4H, $-CH_2-N-$), 3.91 (t, 4H, $-CH_2-O-$), 4.6 (s, 2H, -NH-), 7.17 (s, 2H, aromatic protons).

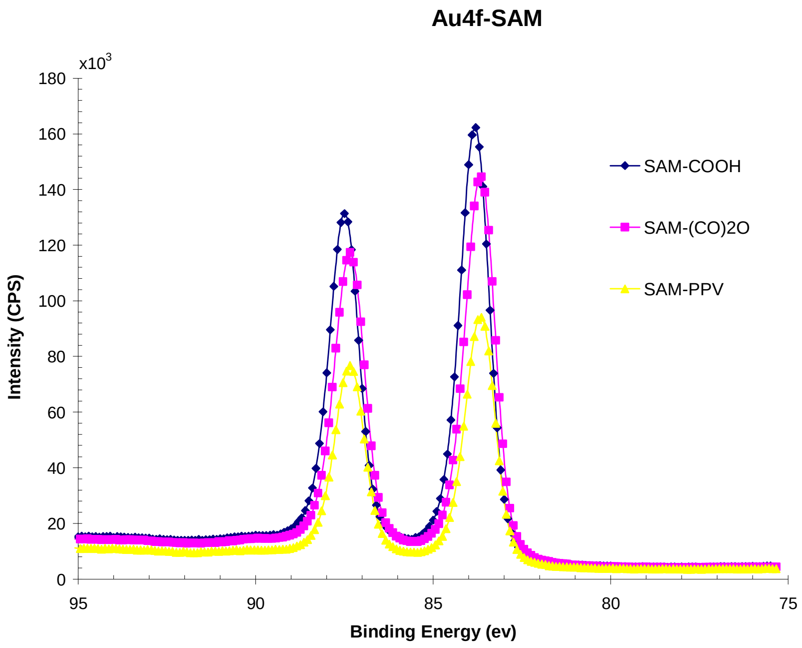
Polymerization. Polymer I: Tri-*n*-butylamine (0.50ml, 2.09mmol) was added the mixture of compound **1** (0.62 g, 0.84 mmol), *p*-divinylbenzene (0.107 g, 0.84mmol), palladium acetate (7.21mg, 0.032mmol), and tri-*o*-tolylphosphine (48.7mg, 0.16 mmol) in 15mL of DMF. The reaction mixture was stirred at 90°C for 6 h under a nitrogen atmosphere and then poured into methanol. The precipitate was collected, redissolved in chloroform, and filtered to remove the catalyst residue. The filtrate was concentrated and precipitated into methanol, followed again by filtration and reprecipitation. The resulting polymer was further purified by extraction in a Soxhlet extractor with methanol for 24 h and then dried under a vacuum at 25°C for 24 h to get 0.40 g orange solid. Anal. Calcd for $C_{36}H_{50}N_2O_6$: C, 71.3; H, 8.24; N, 4.62. Found: C, 72.6; H, 8.04; N, 4.50. *^{1}H NMR* ($CDCl_3$, ppm): δ 1.29 (broad, 18H, $-CH_3$), 1.53 (broad, 8H, $-CH_2-$), 1.83 (broad, 4H, $-CH_2-$), 3.11 (broad, 4H, $-CH_2-N-$), 4.02 (broad, 4H, $-CH_2-O-$), 4.54 (broad, 2H, -NH-), 7.07 (broad, 4H, vinyl protons), 7.19 (broad, 2H, aromatic protons), 7.47 (broad, 4H, aromatic protons).

Polymer II: Trifluoroacetic acid (2 mL) was added to a solution of polymer **I** (250 mg) in 10 mL of CH_2Cl_2. The solution was stirred at room temperature overnight under a nitrogen atmosphere and then poured into methanol. The precipitate was collected by filtration, redissolved in a minimum amount of hot chloroform, and precipitated into methanol. The resulting polymer was extracted with methanol for 24 h and was then dried under a vacuum overnight to get 150 mg dark orange solid. Anal. Calcd for $C_{26}H_{34}N_2O_2$: C, 76.8; H, 8.37; N, 6.89. Found: C, 73.7; H, 8.13; N, 6.56. *^{1}H NMR* ($CDCl_3$, ppm): δ 1.36 (broad, 4H, $-CH_2-$), 1.47 (4H, $-CH_2-$), 1.94 (broad, 4H, $-CH_2-$), 3.19 (broad, 4H, $-CH_2-N-$), 4.08 (broad, 4H, $-CH_2-O-$), 4.62 (broad, 4H, $-NH_2$), 7.17 (broad, 4H, vinyl protons), 7.24 (broad, 2H, aromatic protons), 7.51 (broad, 4H, aromatic protons).

Preparation of the Patterned SAM with Interchain Caboxylic Anhydride. Gold substrates were prepared by evaporating thin films of chromium (100 Å, adhesion-promoting layer) and gold (1000 Å) onto Si wafers. The stamp was fabricated by pouring a 10:1 mixture of Sylgard 184 elastomer / curing agent (Dow Corning, Midland, MI) over a photolithographically prepared silicon master. The PDMS was cured at 50 ^{0}C overnight and then carefully peered away from the master. A 1 mM solution of 16-mercaptohexadecanoic acid (MHA) in absolute ethanol was used to ink the stamp. After evaporation of the solvent, the PDMS stamp was briefly dried under a gentle stream of nitrogen and was brought into contact with the gold substrate for 1 min. The stamp was carefully peeled off, and the substrate was rinsed with absolute ethanol to remove the excess alkanethiol and dried in a stream of nitrogen. The patterned substrates having SAMs of the carboxylic acid were immersed in a freshly prepared solution of 0.1 M trifluoroacetic anhydride and 0.2 M triethylamine in anhydrous DMF at room temperature. After 30 min, the substrates were removed from solution, rinsed thoroughly with CH_2Cl_2, and dried with nitrogen. The substrates of the reactive SAMs were used immediately.

Characterization. The ^{1}H NMR and ^{13}C spectra were recorded on a Bruker AM 300 spectrometer. Molecular weights and distribution of polymers were determined by using Gel Permeation Chromatography (GPC) with a Waters Associates liquid chromatography equipped with a Water 510 HPLC pump, Waters 410 differential refractometer, and Waters 486 tunable absorbance detector. THF was used as the eluent, and polystyrene were used as the standard. Grazing angle FTIR spectra were obtained in single reflection mode using Digilab Fourier Transform Infrared Spectrometer (Biorad, Cambridge, MA). The p-polarized light was incident at 86° relative to the surface normal of the substrate, and a mercury-cadmium-telluride (MCT) detector was used to detect the reflected light. A spectrum of a SAM of n-hexecane-thiolate-d_{18} on gold was taken as a reference. X-ray Photoelectron Spectroscopy analyzes were performed on a Kratos Axis Ultra spectrometer equipped with a monochromoatic Al Kα source. A pass energy of 80 eV and an energy step of 0.1 eV were used for the survey of sample with titled 45 degree. UV-vis spectra were collected by using a Varian Cary 100 UV-Visible spectrophotometer together with DRA-CA-30I sphere accessory for thin film reflectance measurements, and Emission spectra were collected by using a Varian Cary Eclipse spectrophotometer. Optical micrographs of patterned film were taken using a digital camera mounted on an Olympus BX60M microscope. SEM surface morphology of patterned film were imaged by FEI-Philips XL-20 Scanning Electron Microscopy with accelerating voltage-up to 30 keV, EDS lateral resolution-1.0 µm, Spectral resolution-130 eV, Elements detected in EDS-Be-U, EDS Detection limit-0.1 weight %. AFM surface topography of patterned film were mapped with Digital Instruments Dimension 3100 tapping-mode Atomic Force Microscopy with a silicon etched tip.

XPS data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140
120
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95
90
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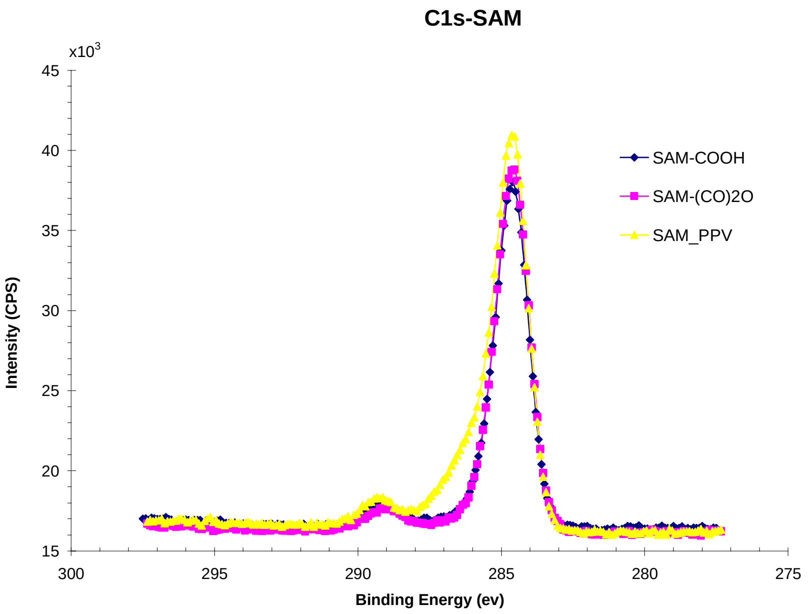
SAM-(CO)2O
SAM-PPV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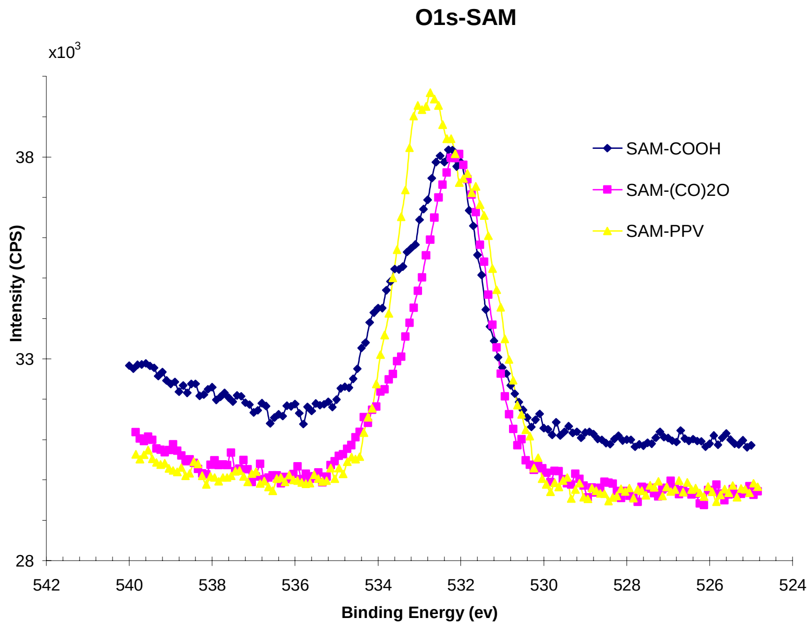
SAM_PPV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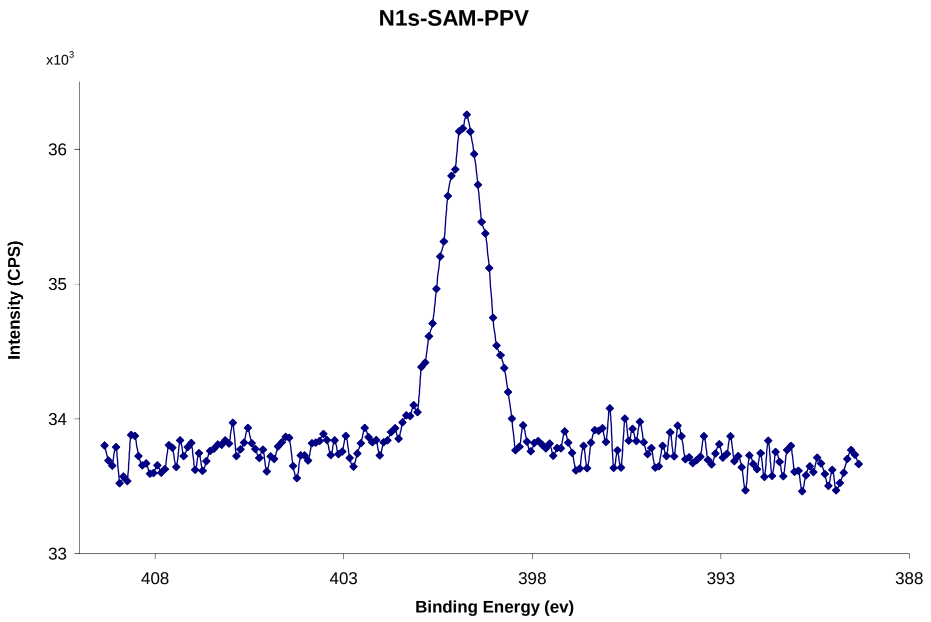
Binding Energy (ev)
SAM-COOH
SAM-(CO)2O
SAM-PPV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393
388
Binding Energy (ev)