Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplemental Materials for

Water-Polyamide Chemical Interplay in Desalination Membranes explored by Ambient Pressure X-ray Photoelectron Spectroscopy

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Preparation & Monomer Building Blocks

Samples were prepared in two setups, one located at Lawrence Berkeley National Laboratory, and the other located at the National Institute of Standards and Technology. Samples in both laboratories were prepared by following the molecular Layer-by-Layer (mLbL) approach presented by Stafford et al..[1,2] In order to obtain very smooth thin films of polyamide, monomer solutions are spin-coated on wafer substrates, alternating between acid and amine building blocks. The concentration of monomer in the solvent should be no higher than 1 %; the samples prepared at NIST using 0.4 % monomer solutions showed improved spatial homogeneity, and comparable surface chemistry. A pure solvent-rinse between each deposition step is crucial for achieving a smooth film. For the rinse after depositing monomer A, toluene was used. For the rinse after depositing monomer B, either acetone or THF were used.

After deposition, some solvent typically remains, which can be allowed to dry out over time or through gentle heating. This drying process results in an increase in the contact angle on the surface. After ~13 days of drying at room temperature, or 15 hrs of drying at ~60 °C, the contact angle stabilizes at 67 ± 11 °, which is in line with observations from literature.

Monomer A contains acid chloride ligands, and monomer B contains amine ligands. Upon contact, a condensation reaction leads to the formation of an amide bond. The choice of trimesoyl chloride (A_3) allows the formation of crosslinks, whereas the choice of terephthaloyl chloride (A_2) produces linear polymer chains. Analogous, m-phenylene diamine can be designated as B_2.

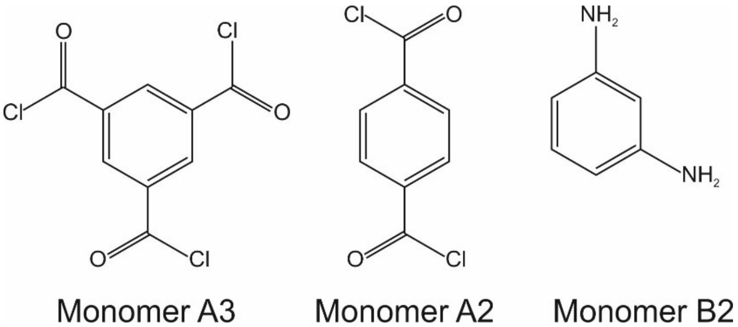

Figure S1: Monomer building blocks for polyamide thin films. A_2 or A_3 is combined with B_2 to form a monolayer.

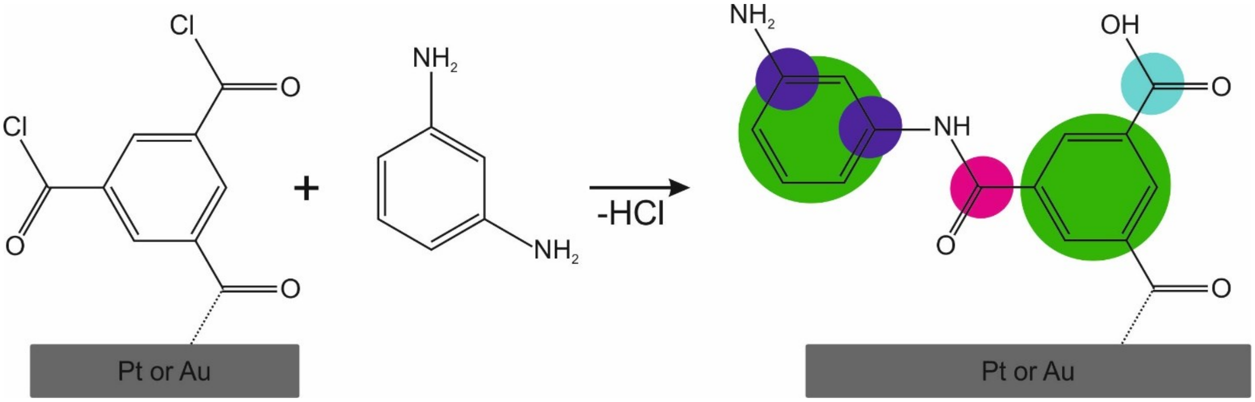

Figure S2: reaction schematic for surface-deposited A3 reacting with B to form a unit of aromatic amide. The color coding of the carbon atoms corresponds to the peak colors in figure 2 of the main manuscript.

Sample overview

designation	cycle number	monomer seq	max RH
PA 7	2.5 ML	ABABA	19% RH
PA 17	7 ML	$(AB)_7$	1.7%
PA 55	1 ML	AB	2% RH
PA56	0.5 Monomer A	A	8% RH
PA63	1.5 ML	ABA	20.5% RH
PA64	1 ML	AB	1.5% RH
Nist0.5A	0.5 Monomer B	B	10% RH
Nist2.5	2.5 ML	BABAB	9% RH

Nist20d	20 ML	$(BA)_{20}$	10%

Reference measurement: water interaction of NH2 chain terminators

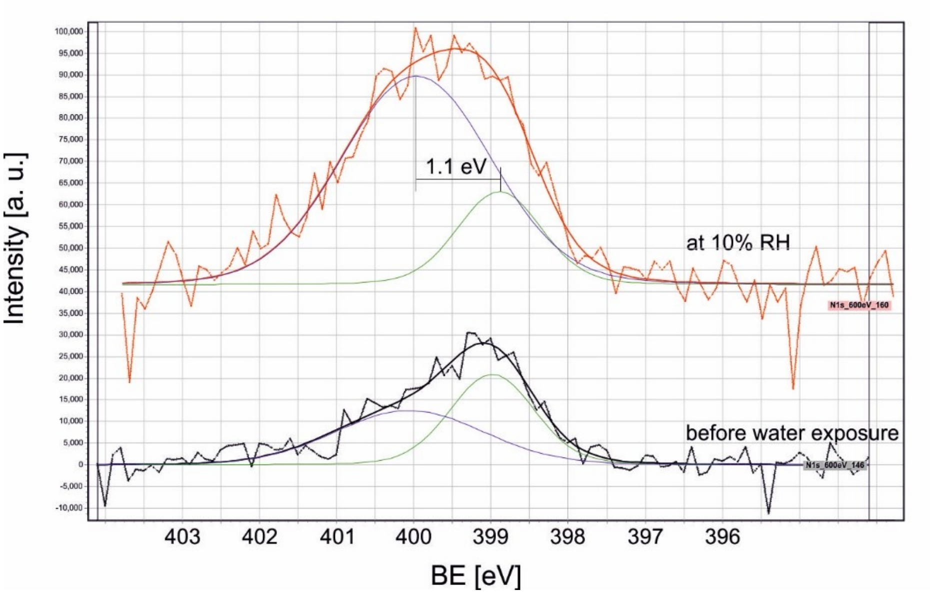

Figure S3: N 1s spectra of a monolayer m-phenylene diamine on Au. Black trace: in UHV at ~50°C. Red trace: in 750mTorr water vapor at 7°C. Traces are vertically offset. Both spectra taken at KE 200 eV.

Shown in Figure S3 is a reference measurement which clarifies the nature of the observed chemical shift in the N 1s spectrum. In the main manuscript, the influence of water vapor on a 2.5 ML thick polyamide film is shown, which contains both amine and amide groups that hypothetically interact with water molecules. Using the spin-coating methodology to produce the thin film samples, the coexistence of the two closely related nitrogen moieties is unavoidable.

The preparation of a sample with only the m-phenylene diamine monomer allows to observation of the interaction of water with only amine groups present on the surface. As shown in Figure S3, two species exist on the sample. When the sample is exposed to increasing relative humidity, the high-BE species increases in relative intensity. This behavior is consistent with the formation of a water-nitrogen complex. The chemical shift between the two species is around 1.1 eV.