

“Layer-by-layer Assembly of Zn(II) and Ni(II) 5,10,15,20-tetra(4-ethynylphenyl)porphyrin
Multilayers on Au using Copper Catalyzed Azide-Alkyne Cycloaddition (CuAAC)”

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Supplemental Information

Experimental

Materials. Solvents, ACS reagent grade or better, were purchased from Sigma Aldrich or Fisher Scientific and used as received. (+)-Sodium L-ascorbate (Aldrich), 4,4'-diazido-2,2'-stilbenedisulfonic acid disodium salt tetrahydrate (**4**) (Fluka), 1-octanethiol (Acros Organics) and 1-dodecane thiol (Aldrich) were used as received. 1-azido-10-decanethiol and 1-azido-18-octadecanethiol were made according to previously published procedures.¹ Zn(II) 5,10,15,20-tetra(4-ethynylphenyl) porphyrin (**1**) and Ni(II) 5,10,15,20-tetra(4-ethynylphenyl) porphyrin (**2**), tris-(benzyltriazolylmethyl)amine (TBTA),² and α,α' -diazideo-p-xylene (**3**)¹ were synthesized according to literature methods. Zn(II) 5-(4-ethynylphenyl)-10,15,20-tri-phenyl porphyrin (**5**) was available from a previous study.³

Au Substrate Preparation. Polished Si(100) wafers (University Wafers: p-type, 1S polished) were cleaned with piranha (1:3 H₂O₂: H₂SO₄ (CAUTION! Strong oxidant reacts violently with organic material!)) for 15 min, rinsed with copious amounts of deionized water and dried under a stream of nitrogen. A 5 nm adhesive layer of Ti was e-beam evaporated first, followed by 100 nm of gold, without breaking the vacuum, using a Temescal e-beam evaporator at base pressure of 5×10^{-7} Torr, and deposition rate of 1.5 Å/s. Film thickness was measured using the IC600 quartz crystal microbalance. Optically transparent Au substrates were prepared in the same manner on piranha cleaned microscope slides, using a 5 nm Ti adhesion layer and 20 nm of Au.

Self Assembled Monolayer Formation. Freshly prepared Au surfaces were cleaned immediately before SAM formation with a UV-ozone cleaner (UV/Ozone Pro Cleaner Plus, Bioforce Nanosciences) for 30 min. The slides were then soaked in 6 M HCl, rinsed with copious amounts of MQ-H₂O, absolute ethanol, and placed in self assembled monolayer (SAM) forming solutions for at least five days. SAMs were made using a 1-azido-10-decanethiol/ 1-octanethiol (diluent) or 1-azido-18-octadecanethiol/ 1-dodecanethiol (diluent) solutions at 0.1mM in absolute ethanol. Before multilayer growth, the Au-SAM substrates were placed in a 100 fold more concentrated SAM forming solution of the same composition overnight. The samples were used for multilayer fabrication immediately after taking out of the SAM forming solution, rinsed with significant amounts of absolute ethanol and dried under a stream of nitrogen.

Porphyrin Multilayer Fabrication. CuAAC reactions on the surface of the azido-SAM Au substrates were carried out in 98.4:0.4:1.2 of DMSO: H₂O: THF. Regardless of the type of the porphyrin its concentration in the surface click reaction was 0.50 mM, CuSO₄ was 0.12 mM, TBTA 0.14 mM and sodium ascorbate 0.25 mM. Similar molar ratios were used for depositing the azido-linker layers.

Electronic absorption spectroscopy. All measurements were performed using Perkin-Elmer Lambda 950 spectrometer. Specular reflectance was performed at a near normal angle of incidence (6° from surface normal). Transmission experiments were done with the same instrument using the optically transparent gold coated microscope slides as substrates in a quartz cuvette filled with de-ionized water.

Spectroscopic Ellipsometry. Spectroscopic ellipsometry was performed using a M-44 WVASE Woolam Ellipsometer at angles of incidence of 55 through 75 degrees, with 5 degree increments. All data analysis was performed with the WVASE32 software. Freshly cleaned Au samples were analyzed first to obtain the optical constants of the substrate for use in subsequent modeling. Multilayer samples of different thicknesses were analyzed using a Cauchy dispersion

model, which described the index of refraction of both the SAM and multilayers components over the transparent region of the film (673.9–741.5 nm), to determine film thicknesses. Once the film thickness had been determined, a point-by-point fit over the whole spectroscopic instrumental range was performed to obtain an initial $n(\lambda)$ and $k(\lambda)$ profile. This spectrum was then used as a reference for the determination of $n(\lambda)$ and $k(\lambda)$ through Kramers–Kronig consistent oscillator modeling using Lorentzian peaks for each of the porphyrin absorptions while holding the thickness constant.⁴

Atomic Force Microscopy. Surface topology of the samples was analyzed with a Digital Instruments Multimode IIIa instrument in the tapping mode using ultrasharp silicon probes NSC14/AIBS from MikroMasch. The cantilevers had a tip radius of curvature of ~10 nm and an average force constant 5.7 N/m (1.8–12.5 N/m range), average resonant frequency ~160 kHz (110–220 kHz range). The root mean squared roughness values were obtained using n-Surf software from 1 $\mu\text{m} \times 1 \mu\text{m}$ height profile images of multilayer films with different number of bilayers.

X-Ray Photoelectron Spectroscopy. XPS data were collected using Physical Electronics PHI 5000 VersaProbe. To account for any charging effects, all of the XPS peaks positions were referenced to the C 1s peak that was fixed at a position of 284.5 eV.⁵ Percent atomic composition was obtained using the Multipak 9.0 software inherent to the instrument. An iterated Shirley background^{6,7} was applied to the Cu2p_{3/2} peaks and they were fit using Gaussian–Lorentz oscillators to deconvolute the Cu(I) and Cu(II) contributions.

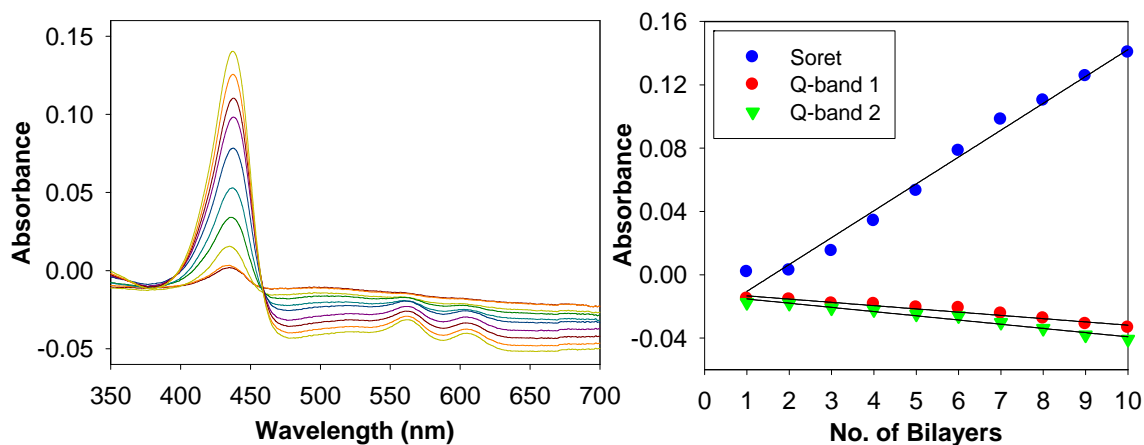


Figure S1. *Left:* UV–Vis of multilayers of **1** and **3** assembled on azide-terminated SAM on optically transparent e-beam evaporated Au. Absorption spectra for porphyrin layers are shown. *Right:* Absorbance vs. the number of bilayers at the Soret and Q-bands illustrate the linear dependence for multilayer growth.

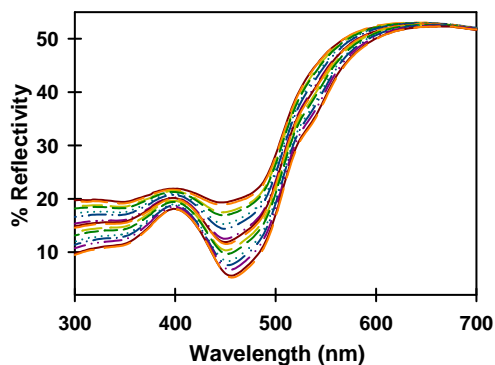


Figure S2. Specular reflectivity scans of 1 through 16 bilayers of **2** and **4** on 100 nm thick Au. Only porphyrin layer spectra are shown for clarity.

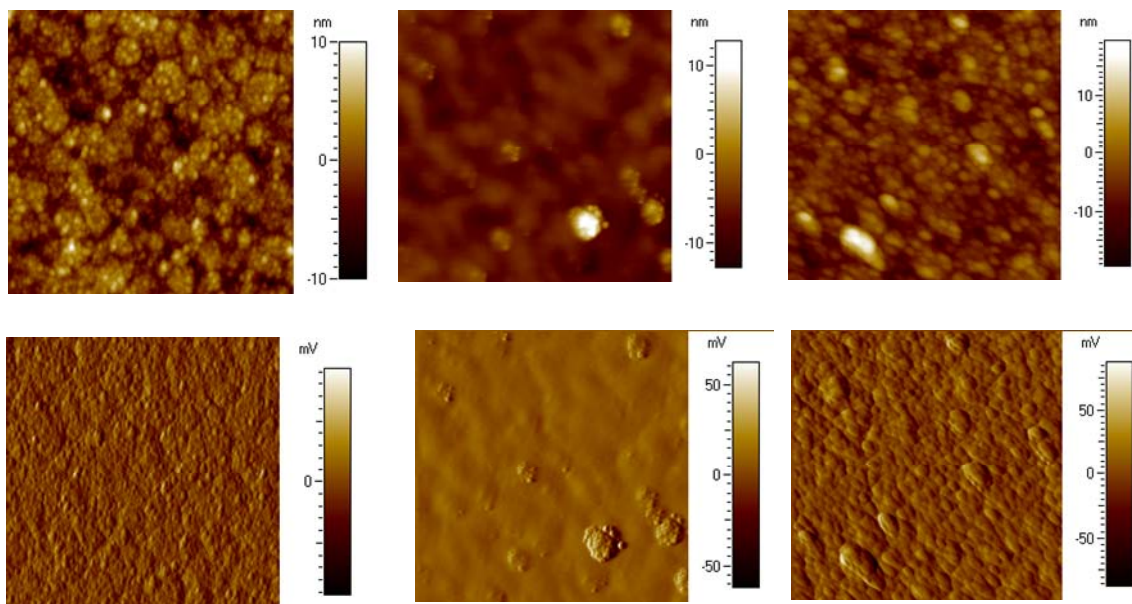


Figure S3. TM-AFM images of 4 (left), 10 (middle) and 16 (right) bilayers of multilayers based on **1** and **4**. The upper images are topography AFM height profile and the lower are amplitude scans, a pseudoderivative of the topography data to emphasize the structural characteristics. All TM-AFM images areas are $1 \mu\text{m} \times 1 \mu\text{m}$. Root mean squared roughness, R_q (nm): 2.5, 2.1 and 3.8 for 4, 10 and 16 bilayers respectively.

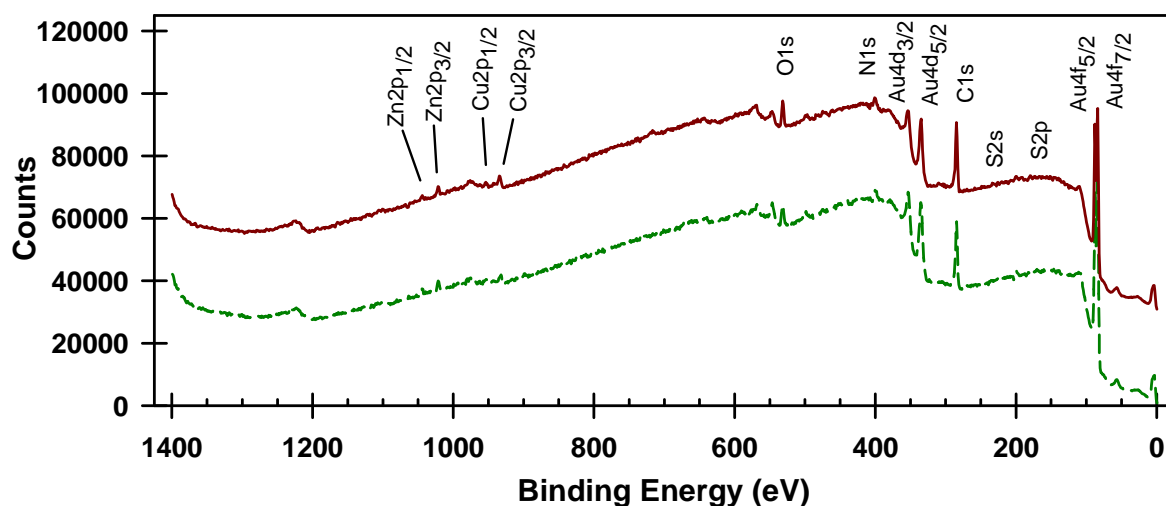


Figure S4. XPS scans of multilayers of **1** and **3** before (green dashed line) and after (red solid line) treatment with Na₂EDTA_(aq).

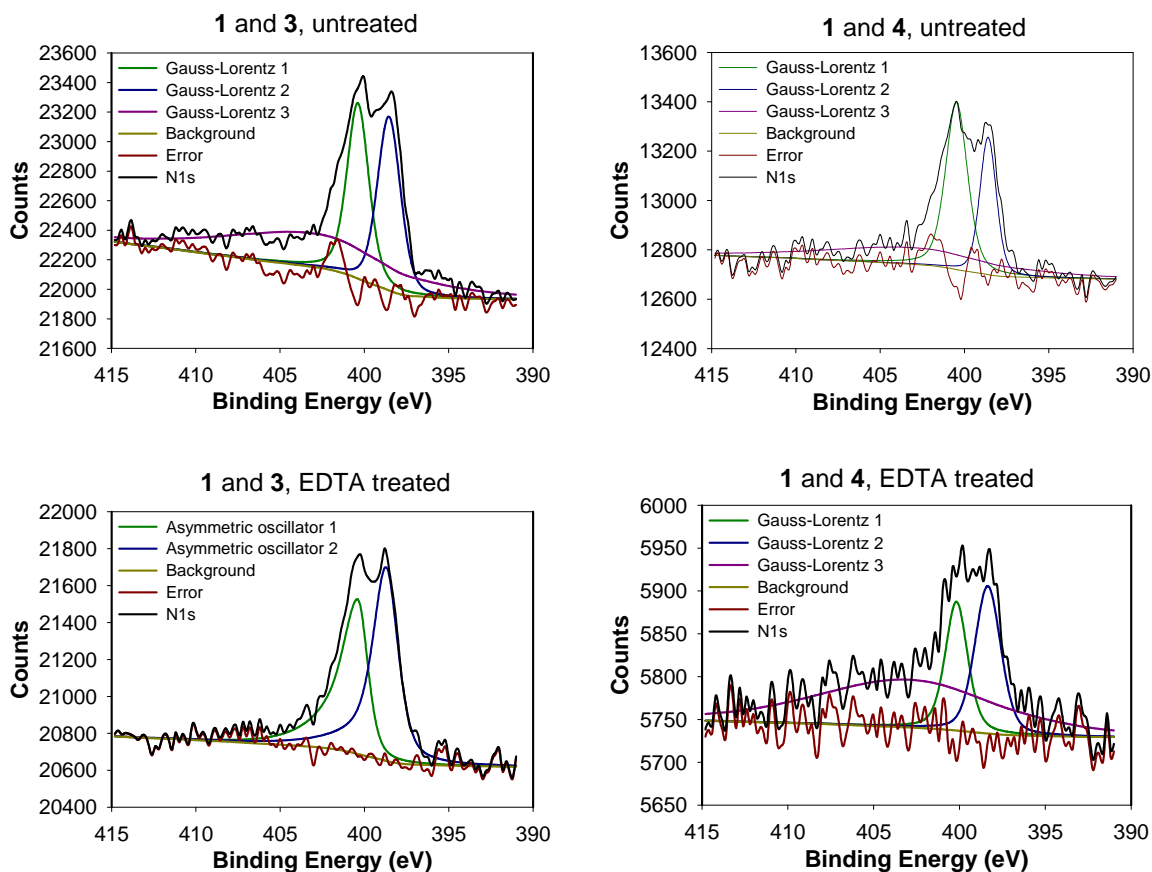


Figure S5. High resolution scans of the N1s peak, with deconvolutions, for multilayer films of **1** and **3** (left) and **1** and **4** (right) before (top) and after (bottom) treatment with Na₂EDTA_(aq).

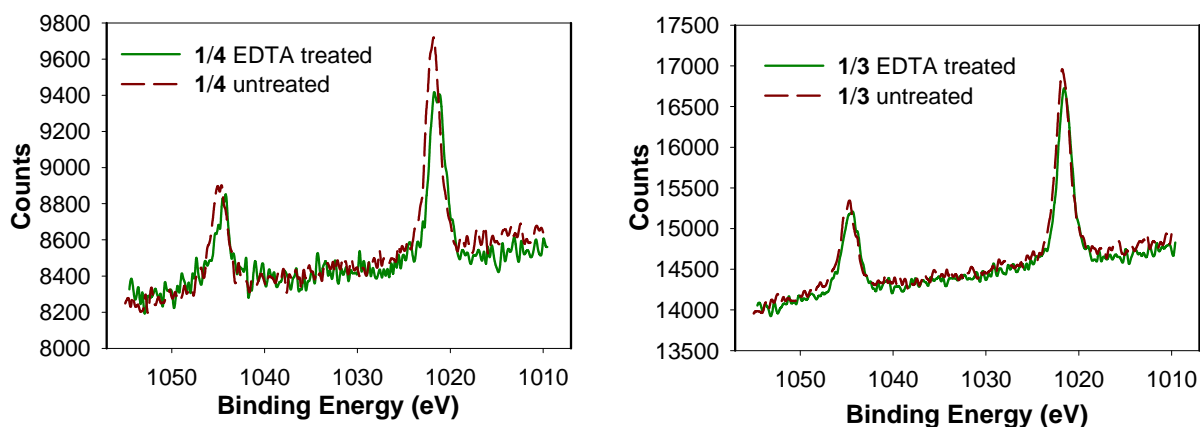


Figure S6. High resolution scans of the Zn_{2p_{1/2}} and Zn_{2p_{3/2}} peaks for multilayer films of **1** and **3**, and **1** and **4** before (dashed line) and after (solid line) treatment with Na₂EDTA_(aq).

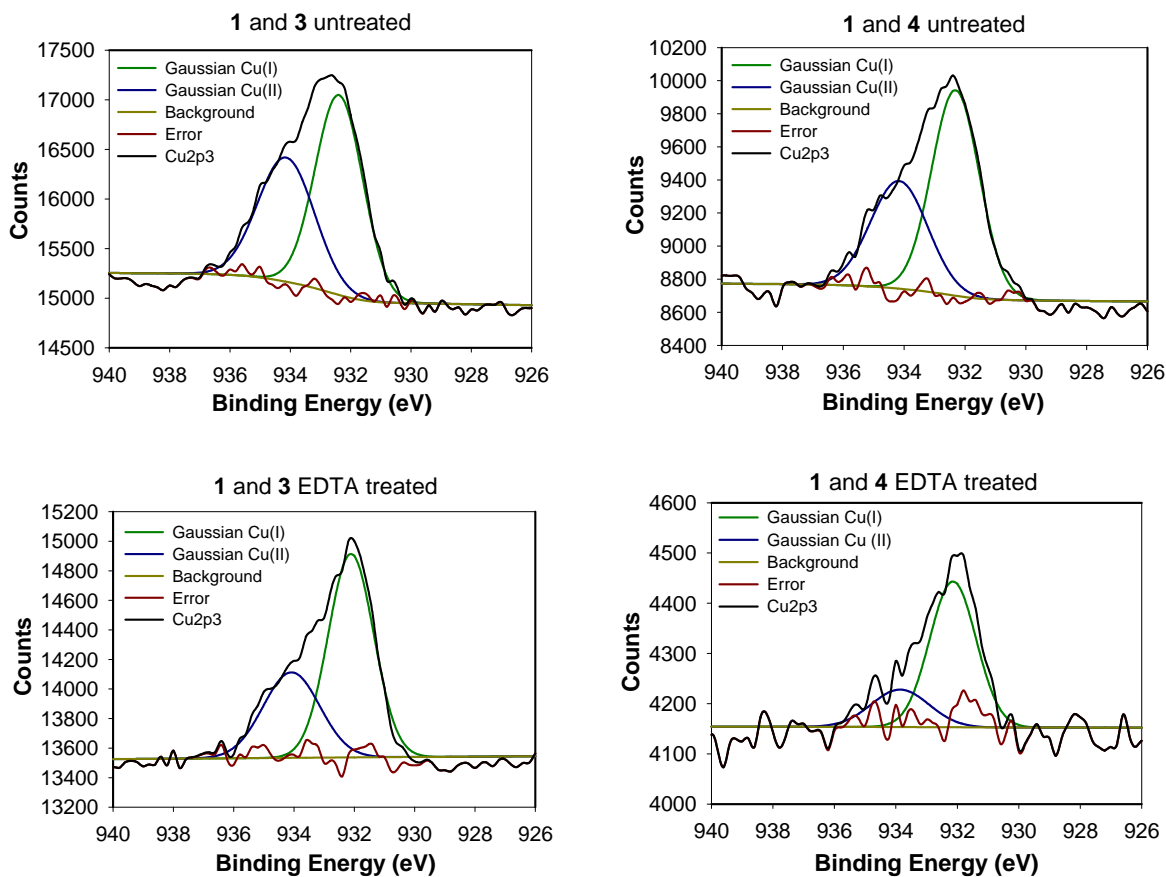


Figure S7. High resolution scans and deconvolution of the Cu_{2p_{3/2}} peak for multilayer films of **1** and **3**, and **1** and **4** before (dashed line) and after (solid line) treatment with Na₂EDTA_(aq).

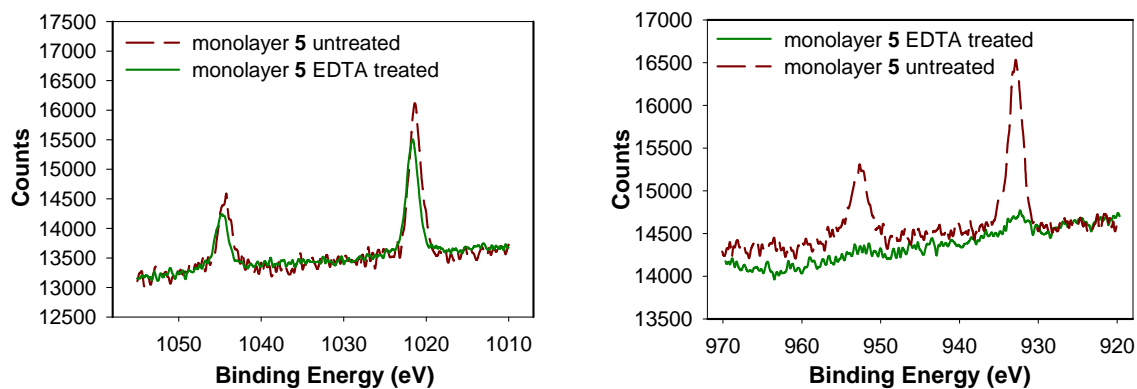


Figure S8. High resolution scans for a monolayer of **5** on azido-terminated SAM on Au(111) before (dashed line) and after (solid line) treatment with $\text{Na}_2\text{EDTA}_{(\text{aq})}$. Left plot covers the $\text{Zn}2p_{1/2}$ and $\text{Zn}2p_{3/2}$ peaks and right, the $\text{Cu}2p_{1/2}$ and $\text{Cu}2p_{3/2}$ peaks