Supporting Information

Synthesis and Characterization of Perylene Diimide–Based Molecular Multilayers Using CuAAC: Towards Panchromatic Assemblies

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Figure S1. The peak absorbance of each PDI obtained during multilayer growth. Data taken from the spectra in Figure 1. Top: **PhO-PDI** at 520nm. Middle: **Thiol-PDI** at 565nm. Bottom: **Pyrr-PDI** at 730nm.



Figure S2. The peak absorbance of **Thiol-PDI** at 565 nm (top) and **Pyrr-PDI** at 730 nm (bottom) as a function of polarization angle of the incident light and the angle of the slide with respect to the light path (red triangles are data with slides at 90° to incident light, pink squares at 60° and blue circles at 45°).



Figure S3. GATR-FTIR spectra obtained during multilayer growth of **PhO-PDI** (left) and **Thiol-PDI** (right) on ITO electrodes.



Figure S4. The integrated IR absorbance intensity of the azide vibrational mode at 2100cm⁻¹ (left) and the two carbonyl vibrational modes at 1700cm⁻¹ and 1670cm⁻¹ (right) as function of layer addition determined by GATR-FTIR. Half-integer layers are azide terminated (azido-SAM or N₃Mest) and full integer layers are following a reaction with **PhO-PDI** (red circles) and **Thiol-PDI** (blue triangles).



Figure S5. Cyclic voltammograms of one through five bilayers of **Pyrr-PDI** assembled on an ITO electrode. CVs were obtained at scan rate of 1 V/sec with 0.1M TBAP in anhydrous acetonitrile as the electrolyte. The arrow shows the initial scan direction. The small peaks prior to both anodic and cathodic waves are likely due to electro-polymerization of the PDIs in the film. These only appear when CVs proceed anodically past +0.1 V vs Fc^{0/+}.



Figure S6. The integrated charge per layer for each of the three PDIs from scans of subsequent bilayers on an ITO electrode surface scanned at 1 V/sec in 0.1M tetrabutylammonium hexafluorophosphate in acetonitrile.



Figure S7. Plots following the maximum wavelength absorptions of each of the perylenes. Layers 1-5 were grown using the **PhO-PDI**, layers 6-10 were grown using **Thiol-PDI** and the last layers, 11-15 were grown using **Pyrr-PDI**. (a) Plot following absorption maximum of **PhO-PDI** at 520 nm which grows strongly in layers 1-5 and tails off in the subsequent layers. (b) Plot following maximum absorption of **Thiol-PDI** at 565 nm, which shares a shoulder absorption of Pho-PDI and thus grows linearly in layers 1-5, but then grows again in layers 6-10 due to the strong **Thiol-PDI** absorption. (c) Plot tracking the growth of **Pyrr-PDI** with maximum absorption at 730 nm that grows slowly in absorbance for layers 1-10 and then strongly in the last five layers.