Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information for

Visualizing nanoscale heterogeneity in perylene thin films *via* tip-enhanced photoluminescence with unsupervised machine learning

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Experimental

Sample preparation. Thermal evaporation technique was used to grow the films of PTCDI (Luminescence Technology, > 99%) molecules on ultra-flat highly oriented gold substrates. The deposition was carried out in a UHV with a base pressure of 1×10^{-9} Torr and at room temperature. The rate of deposition and thickness of PTCDI films were monitored by a quartz crystal microbalance.

Ultraviolet photoemission spectroscopy (UPS):

To determine the band alignment at the PTCDI/Au interface, UPS measurements were conducted on two samples: i) Au (111) surface and ii) 5 nm PTCDI grown on the Au (111) substrate. The Au(111) surface was prepared by standard sputtering and annealing cycles. The PTCDI was deposited on Au in an ultra-high vacuum (UHV) chamber using thermal evaporation. The two spectra are shown in Fig. S1. The highest occupied molecular orbital (HOMO) level relative to the Fermi level (E_f) is determined from the spectral region near the E_f, Fig. S1b. The vacuum levels are determined from the secondary electron cutoff (SECO), Fig. S1a. The lowest unoccupied molecular orbital (LUMO) level of PTCDI is determined by using optical band gap of 2.2 eV

The UPS measurements were conducted in an ultra-high vacuum (UHV) chamber at a base pressure around 1×10^{-10} Torr. The He-I emission line (21.22 eV) from a standard UV lamp was used for the photoemission. A hemispherical analyzer with an imaging detector (Phoibos 100, SPECS) was used to measure the kinetic energy of photoelectrons.

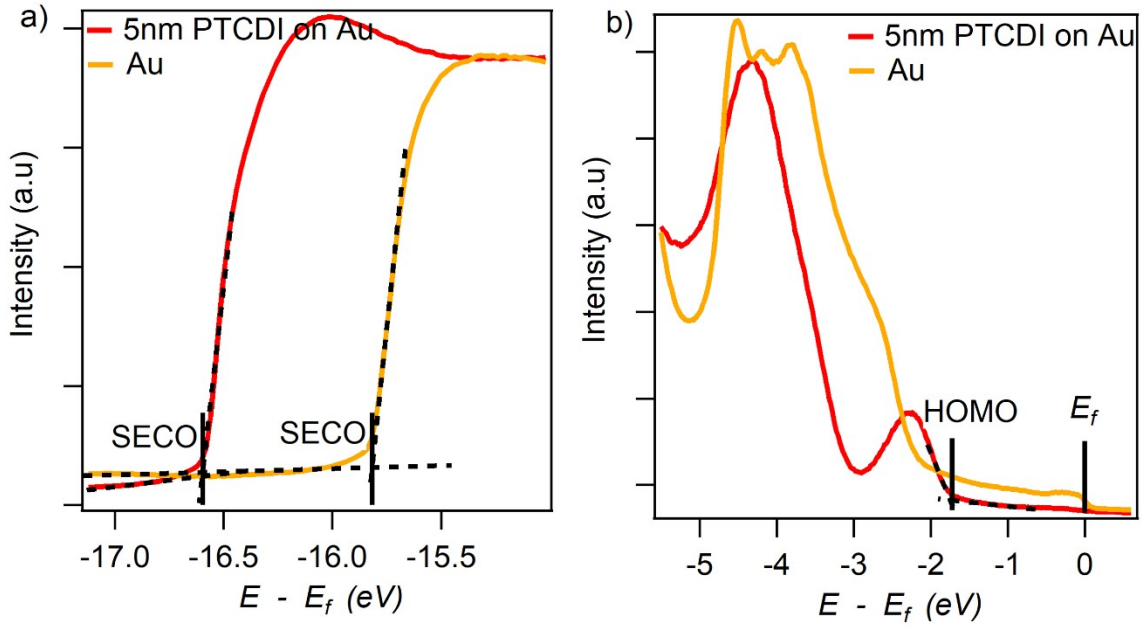

Figure S1: UPS spectra showing (a) the SECO region and b) the region near the Fermi level.

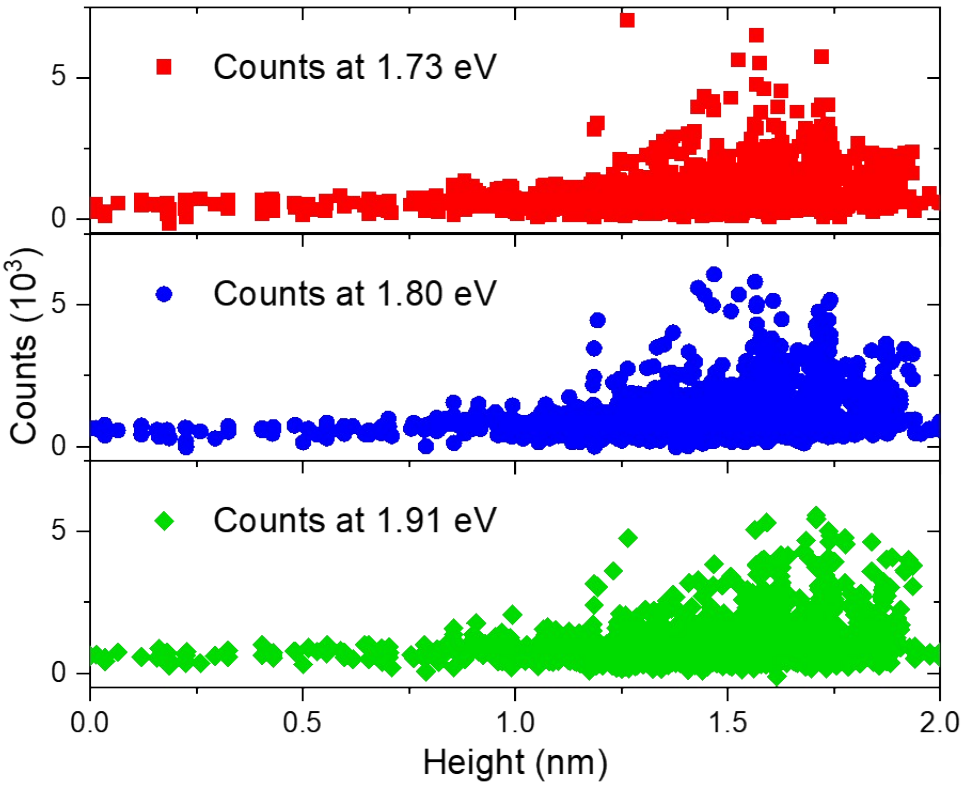

Figure S2: Intensity (counts) versus height at different energies corresponding to different physical processes.

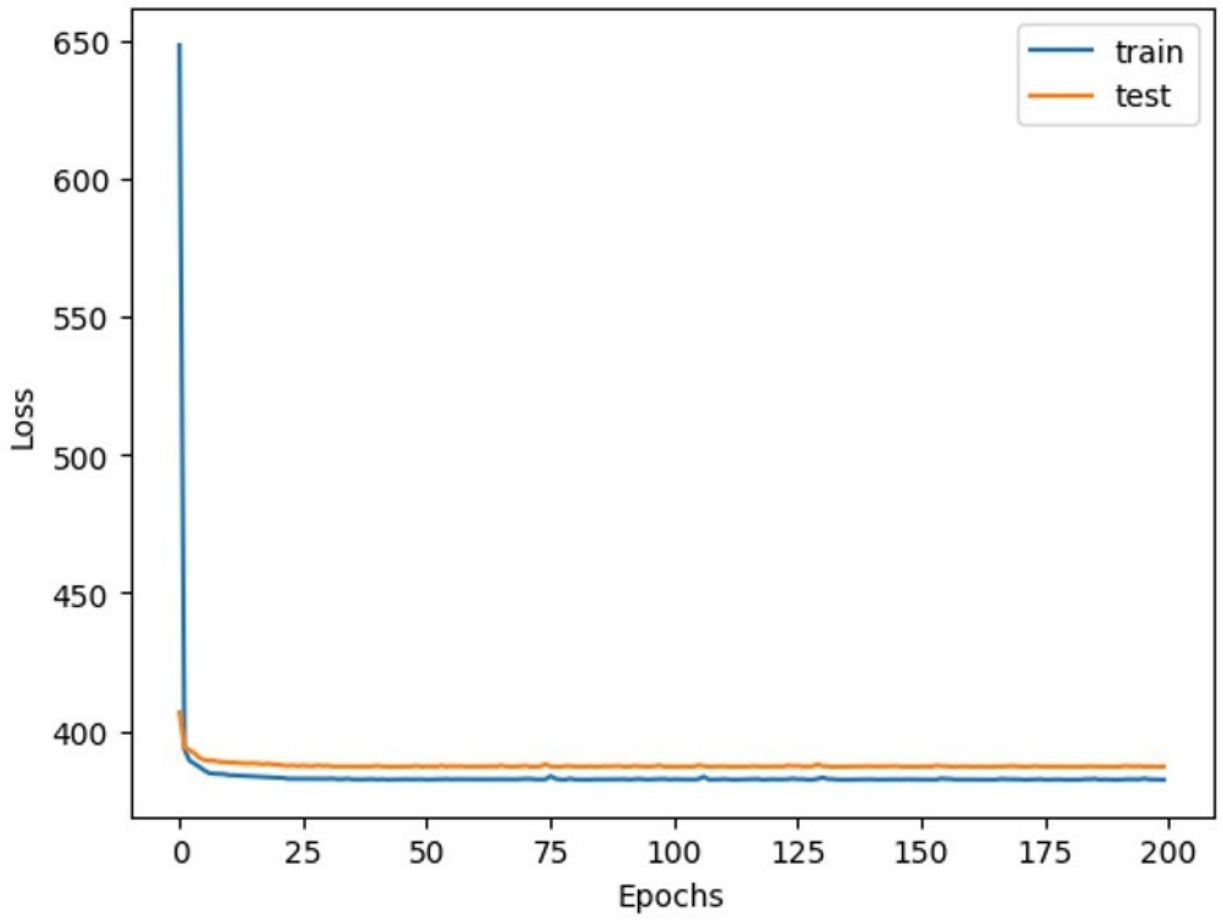

Figure S3: Train and test loss curves that show no indication of overfitting.

ML/Data Analysis. In our implementation, we utilized standard architectures of the encoder and decoder neural networks. The encoder starts with a feature extraction stage using 1D convolutional layers and rectified linear unit activation functions to progressively extract and refine features from the input data. This is coupled with the downsampling process, effectively capturing dominant features while reducing dimensionality. The extracted features are then transformed into a lower-dimensional latent space through a fully-connected layer. On the other side, the decoder begins by expanding the condensed latent representation back to a higher-dimensional space using a fully-connected layer. It then employs a series of upsampling and convolutional layers, mirroring the encoder but in reverse order. These layers gradually increase the spatial dimensions reconstructing

the data back to its original form. The training focuses on minimizing a loss function that includes reconstruction error and Kullback-Leibler regularization term, aiming at precise input reconstruction and a coherent, structured latent space that captures the fundamental variations and characteristics of the data.

The analysis is available @ https://github.com/ziatdinovmax/OpticalNanoImagingML

AFM and TEPL. Topographic and nano-optical mapping was performed as described in a recent work (ref. 12 in the main text). Specifics are otherwise given in the main text and figure captions.