## Diffractive X-ray waveguiding reveals orthogonal crystalline stratification in conjugated polymer thin films

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The depth dependence of crystalline structure within thin films is critical for many technological applications, but has been impossible to measure directly using common techniques. In this work, by monitoring diffraction peak intensity and location and utilizing the highly angle-dependent waveguiding effects of X-rays near grazing incidence we quantitatively measure the thickness, roughness and orientation of stratified crystalline layers within thin films of a high-performance semiconducting polymer. In particular, this diffractive X-ray waveguiding reveals a self-organized 5-nm-thick crystalline surface layer with crystalline orientation orthogonal to the underlying 65-nm-thick layer. While demonstrated for an organic semiconductor film, this approach is applicable to any thin film material system where stratified crystalline structure and orientation can influence important interfacial processes such as charge injection and field-effect transport.

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