SOCIETY FOR NATURAL SCIENCES STUDENT JOURNAL

Society for Natural Sciences Student Conference
University of Bath 8-9 April 2026

The Latest Techniques for Determining Molecular Orientation on Surfaces

Eleanor Dilks* and Dr Jonathan Ward

Lancaster University Chemistry Department

Introduction

Self-assembled monolayers (SAMs) of dipolar molecules or absorbed molecular acceptors on electrode materials can be used in state-of-the-art optoelectronic devices.[1] For example, to modify indium tin oxide anodes to improve the performance of organic light emitting devices. [2]

The correct orientation of the optical transition dipole moment vectors of the molecules with respect to the substrate plane is paramount for the function and efficiency of the devices. [3] XPS and other techniques can be used to determine the orientation of these molecules; however, no single technique is currently able to determine this successfully and each technique has limitations.

X-ray Photoelectron Spectroscopy (XPS)

XPS is a type of electron emission spectroscopy that gives information about the compositions of surfaces with up to 10 nm depth. X-rays bombard the surface of the material and electrons are emitted. The energy of the electrons emitted depends on the binding energy of the electron, the kinetic energy and the spectrometer work function. The peaks produced can tell you about the element which the electron is emitted from, and its environment. [4]

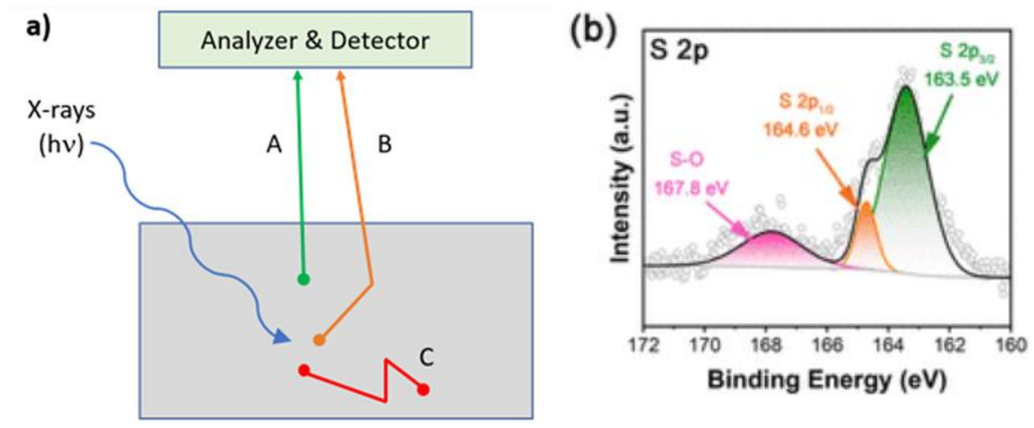


Figure 1. a) The x-rays interact with the sample differently depending on the depth from which they are generated. A: electrons emitted without interaction, B: electrons that undergo at least one inelastic collision, C: electrons that undergo multiple collisions and do not escape the sample. [5] b) An example of an XPS spectra of S 2p core electrons. [6]

XPS can be measured with angular resolution, which adjusts how deep the x-rays can go before the electrons are ejected. When the angle of observation increases, the intensity of the electrons emitted from shallower layers increases and from deeper layers decreases. [5] By measuring at different angles, we gain information about the depth of different atoms within a molecule, with respect to the surface, and therefore its orientation.

Figure 2. X-rays enter the sample and electrons are emitted from different depths depending on angle.

Other Techniques

Other techniques for determining molecular orientation on surfaces include, near-edge x-ray absorption fine structure (NEXAFS) spectroscopy and atomic force microscopy (AFM).

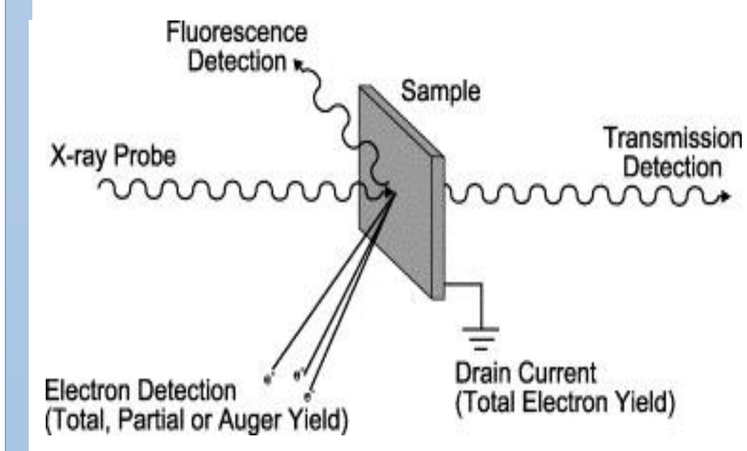


Figure 3. The possible measurement techniques for NEXAFS spectroscopy. [10]

NEXAFS allows the measurement of linear dichroism when the incident angle of polarization is varied. This allows molecular orientation to be determined due to the transitions of electrons being governed by dipole selection rules. [7] Although this is a useful and extremely powerful technique, it requires a synchrotron radiation facility, so its use is less common than XPS. [8]

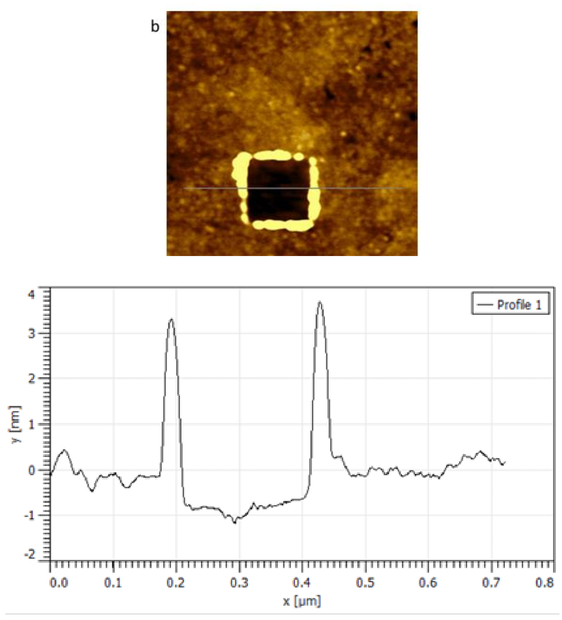


Figure 4. AFM nano-scratching of gold, and the cross-section data. [11]

AFM is a technique which uses surface etching and can measure step height and gain information about thickness, morphology and mechanical properties of SAMs. [9] This could prove useful in conjunction with XPS. However, using this technique alone doesn't give any information about the chemical composition of the SAMs.

Project objectives

Currently, the information depth of XPS is around 10 nm, as 95% of electrons escape from a depth of 10 nm or less.[4] To help resolve this issue, the synthesis of several molecules with XPS active atoms at precise sites, followed by their assembly on a gold surface and analysis by angle-resolved XPS is proposed. The oligophenylene ethynylene (OPE) molecule arrangement is known to stand upright, but this will need to be confirmed for these molecules.

The proposed synthesis (Figure. 5) starts from commercially available materials and uses a Sonogashira coupling to create a molecule which can be assembled in a monolayer and analysed by XPS. Alkyne 1 can be made by three steps from literature methods and commercially available starting materials. [12] [13]

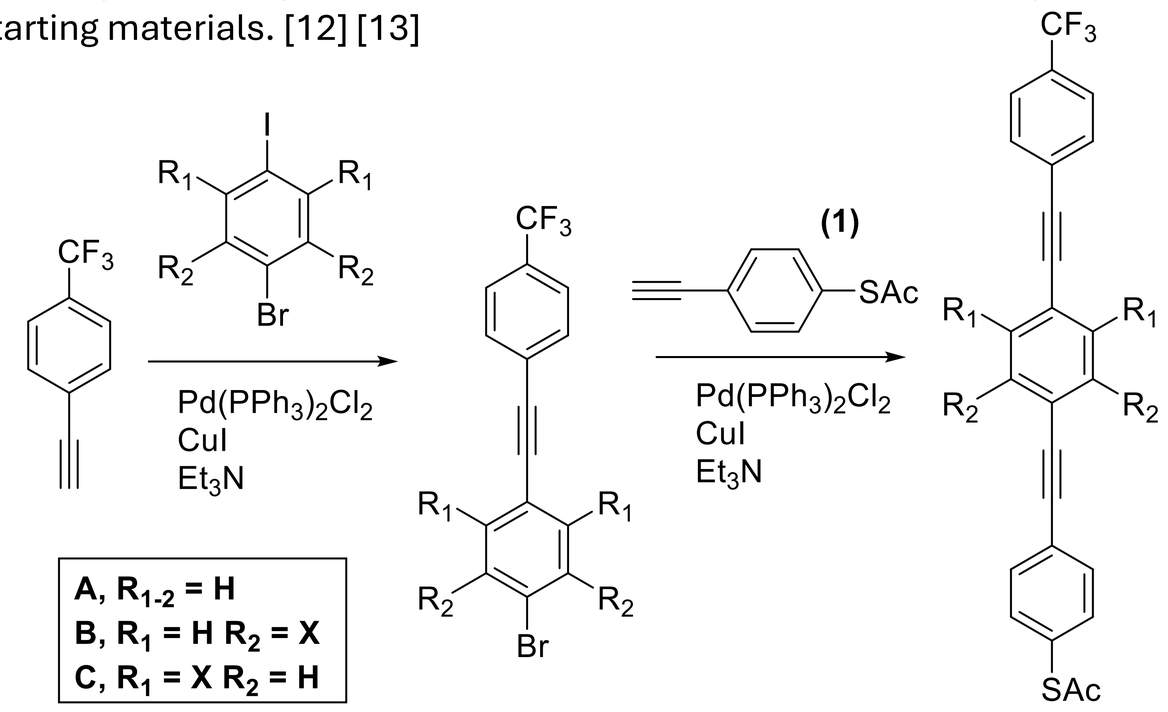


Figure 5. Proposed synthesis pathways for this project.

References

1. Timpel, M., et al., Adv. Funct. Mater., 2018. **28**(8): p. 1704438.
2. D. An, H. Liu, S. Wang and X. Li, *Applied Physics Letters*, 2019, **114**.
3. T. D. Schmidt, T. Lampe, D. Sylvinson M. R, P. I. Djurovich, M. E. Thompson and W. Brütting, Phys. Rev. Appl., 2017, ***8, 037001.***
4. Stevie, F.A. and C.L. Donley, J. Vac., Sci. Technol., A, 2020. **38**(6): p. 063204.
5. Alharbi, A.R.M., et al., Langmuir, 2024. **40**(36): p. 18925–18941.
6. 6. Yang, N., et al., ACS Sustainable Chem. Eng., 2025. **13**(3): p. 1378–1390.
7. Völkner, J., M. Klues, and G. Witte, J. Phys. Chem. C, 2018. **122**(29): p. 16810–16820.
8. Zharnikov, M., J. Electron. Spectrosc. Relat. Phenom., 2023. **264**: p. 147322.
7. Gao, X., et al., Surf. Interfaces, 2024. **46**: p. 104133.
8. Watts, B., L. Thomsen, and P.C. Dastoor, J. Electron. Spectrosc. Relat. Phenom., 2006. **151**(2): p. 105–120.
9. L. J. O'Driscoll, X. Wang, M. Jay, A. S. Batsanov, H. Sadeghi, C. J. Lambert, B. J. Robinson and M. R. Bryce, Angew. Chem., Int. Ed. Engl., *2020, **59, 882–889.***
10. Moreno-García, P., et al., J. Am. Chem. Soc, 2013. **135**(33): p. 12228–12240.
11. Soria-Castro, S.M., et al., J. Org. Chem., 2017. **82**(21): p. 11464–11473.