Scanning Transmission X-ray Imaging Microscopy at ALS Beamline 5.3.2

David Kilcoyne

ALS Scientific Support Group

NEXAFS Spectromicroscopy

Bending Magnet beam line 5.3.2
Scanning Transmission X-Ray Microscope

STXM @ 5.3.2

Examples of Energy Storage Research at 5.3.2

Conclusion and the Future

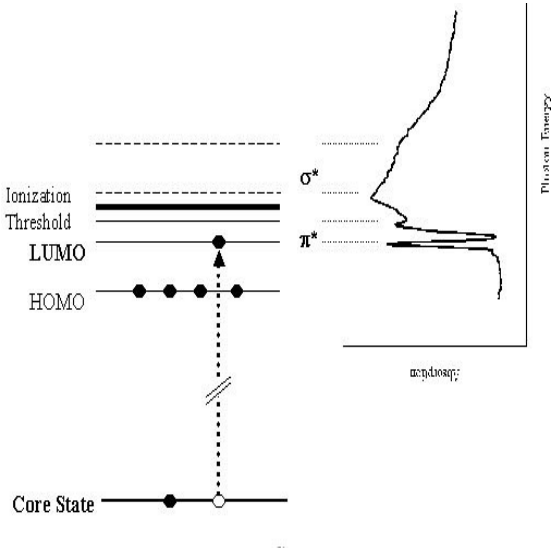
Near Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS) forms the basis for high spatial and energy resolution in X-ray microscopy.

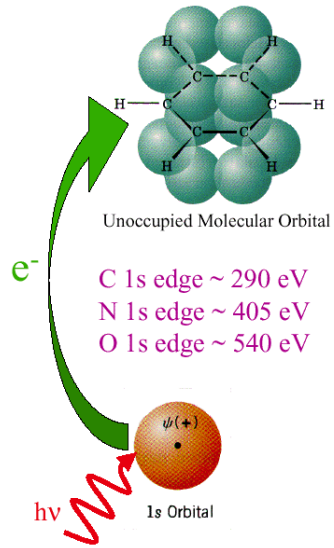
X-ray microscopy is one of the rapidly growing techniques that utilise the unique capabilities of Synchrotron Radiation to characterise and investigate materials. This characterisation method is complementary to X-ray photoemission, absorption and fluorescent spectroscopies.

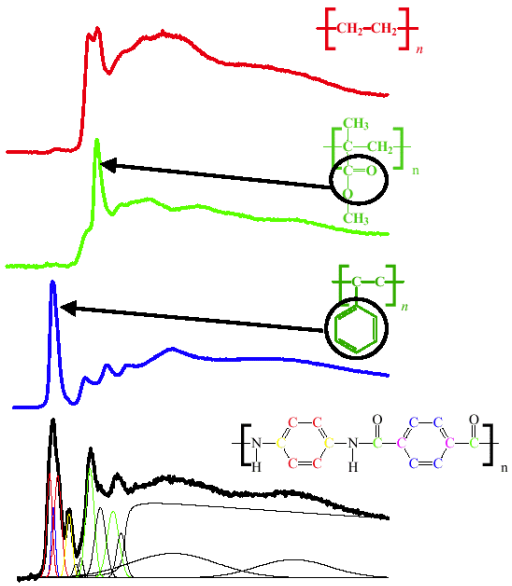
Advances in these spectroscopies have now been extended and complemented, to provide high spatial resolution spectroscopy to investigate heterogeneous and homogeneous material.

The combination of energy dependent spectroscopy with microscopy has resulted in spectromicroscopy – the generation of images with spectral content together with property mapping to images from very small areas.

Near Edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy

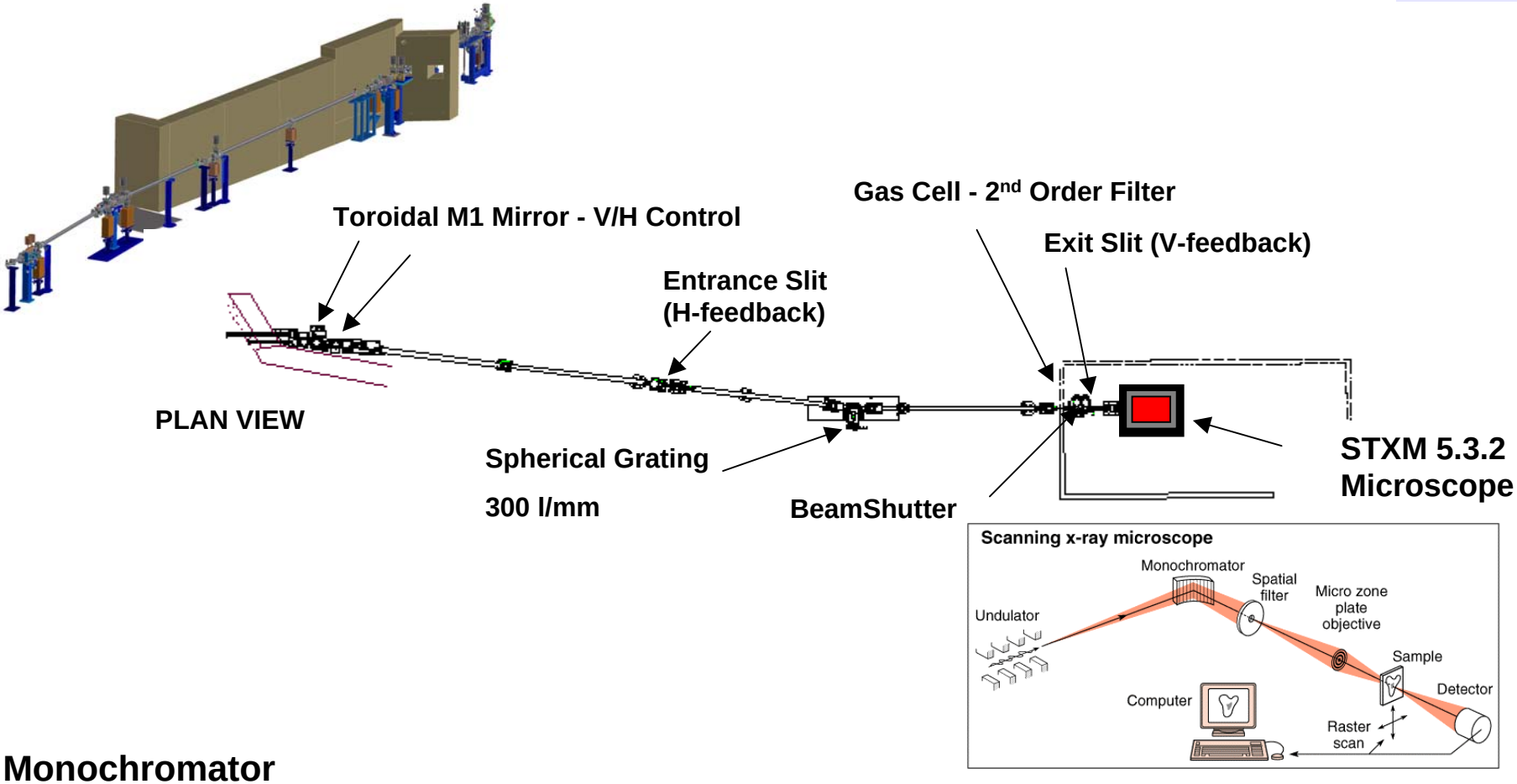






- **NEXAFS Spectromicroscopy – use energies straddling absorption edges to map the distribution of a specific element in the specimen**
- **Imaging with spectral sensitivity and with synchrotron radiation to probe materials at the nanometer level ~ 20 - 30 nm and < 100 nm**
- **Elucidate physical (structural) and chemical properties of polymers, complex materials, extra-terrestrial and environmental samples**
- **Determine chemical site specificity and sensitivity on a quantitative scale**
- **Correlation and complementarities with other techniques – NMR, Raman, IR,…**

ALS Bending Magnet Beam line and Monochromator at 5.3.2



Monochromator

Spherical Grating monochromator (300 l/mm) and a Toroidal M1 mirror with V/H control

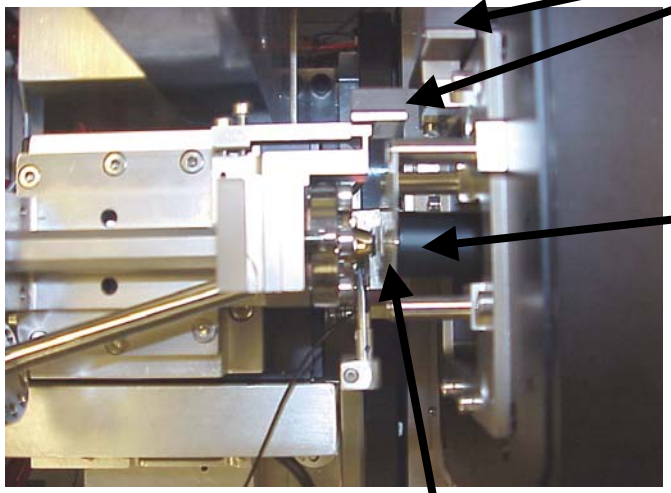
Photon energy range from (160) 250 eV to 800 eV

Energy resolution < 70 meV at the C-edge (slits)

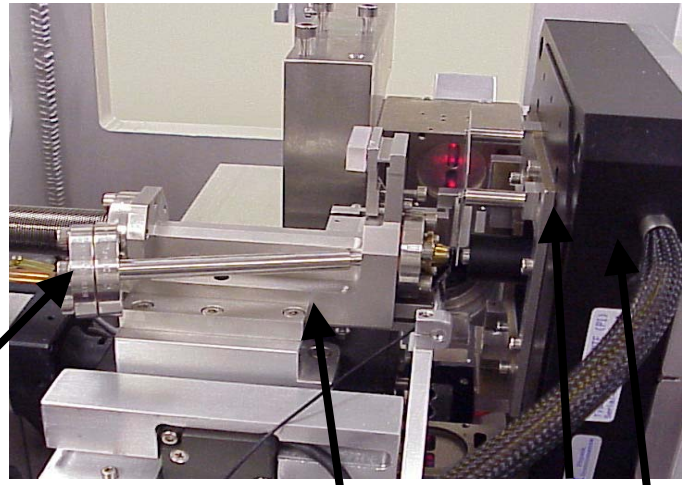
Excellent computer controlled feedback on M1 mirror for stable illumination of the optics and therefore the data and science resulting

Scanning Transmission X-Ray Microscope @ 5.3.2

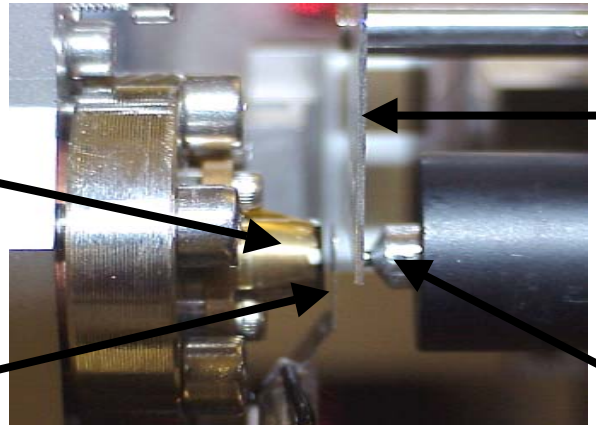
Top View



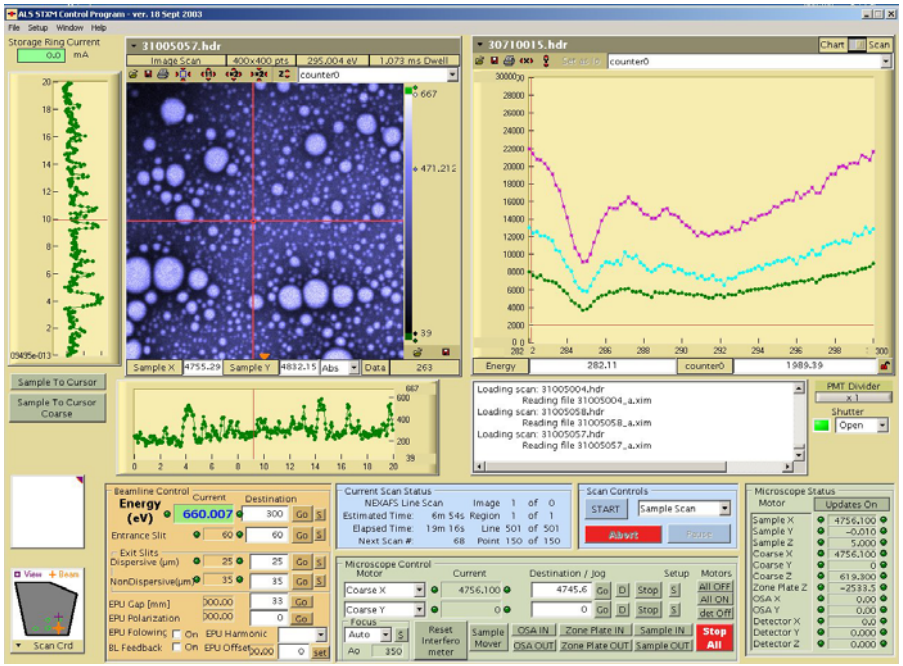
Oblique Side-View

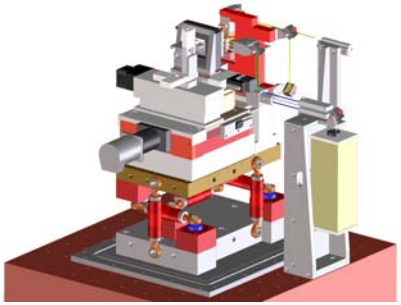


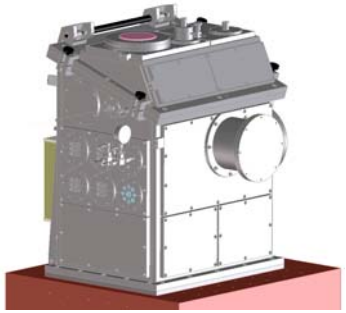
Close-Up Side-View



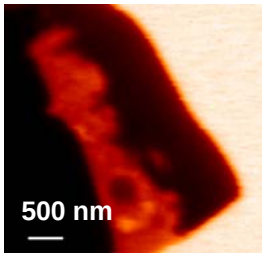
Control and Graphical User Interface for the STXMs @ the ALS

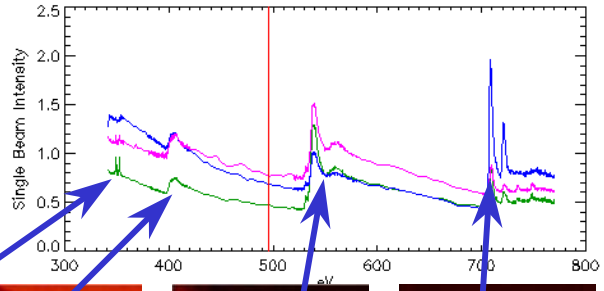


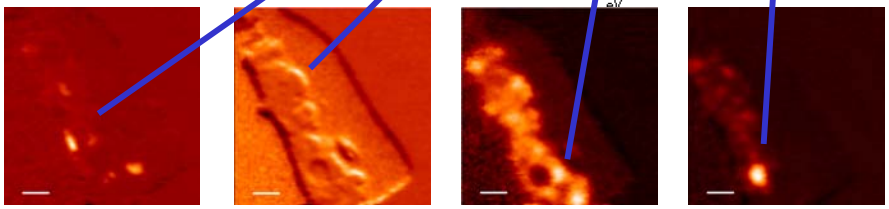




STARDUST PROJECT
Stardust sample l2054-E1-B, from comet Wild 2/81P
Relating stardust to planetary meteorites

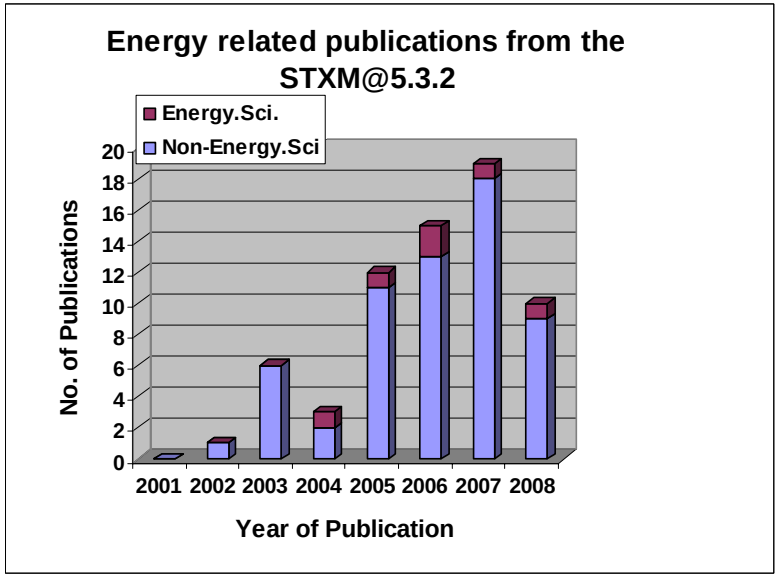


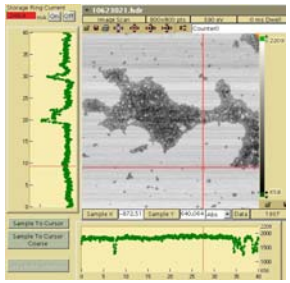




- **Spatial resolution < 30 nm**
- **Excellent S/N with stable beam**
- **Multi-mode data acquisition: multi-image/energy sequences**
  line spectra
  multi-point/energy spectra
- **GUI on both STXMs appears the same to the users – skills learnt easily adapted to the other instrument**
- **Available at both a bending magnet (5.3.2) and/or an EPU source (11.0.2)**

Current energy related science research





2001 – : First STXM image at 5.3.2

2002 – 1 : Beamline Paper

2003 – 6 : STXM Instrumentation Paper

2004 – 3 (1) : Science 1

2005 – 12 (1) : Appl. Phys. Letts. 1

2006 – 15 (2) : Science 2, Phys. Rev. Letts. 1, Nano Letts. 1, Appl. Phys. Letts. 3, Chem. Phys. Letts. 1

2007 – 19 (1) : Nano Letts. 1, Geophys. Res. Letts. 1

2008 – 10 (1) : Earth Pla. Sci. Letts. 1

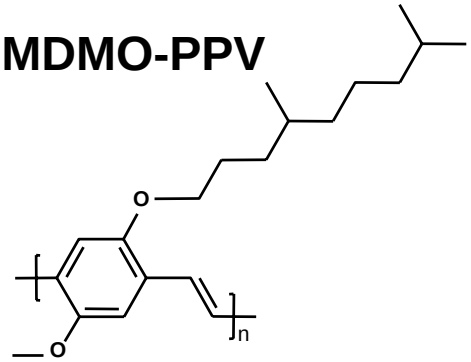
- In-situ spatial and time resolved electrochemcial reactions using STXM
- X-ray microscopy of photovoltaic polyfluorene blends: relating nanomorphology to device performance
- Reverse osmosis composite membrane structures for producing chemical gradients

X-ray Microscopy of Organic Solar Cells

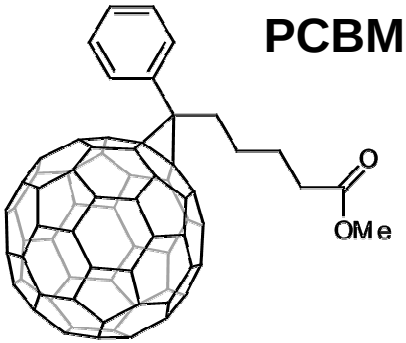
Paul Dastoor (University of Newcastle) , Chris McNeill (University of Cambridge)

- Organic solar cells based on thin-film blends of a conjugated polymer and fullerene are a promising low-cost photovoltaic technology.
- The blend film is solution-processed from a solution containing both species.
- As the film dries, however, it phase separates into “polymer-rich” and “fullerene-rich” phases.
- Being able to quantitatively determine local blend composition is critical to understanding device operation and future optimization.

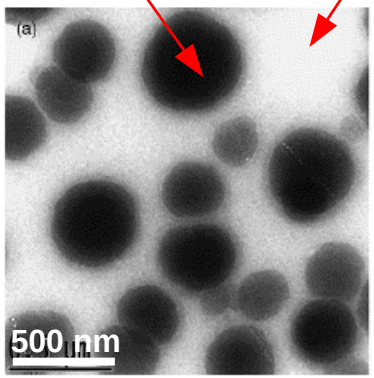
MDMO-PPV



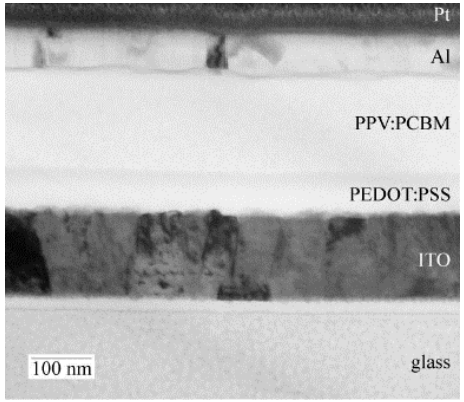
PCBM



“Fullerene-rich” “Polymer-rich”



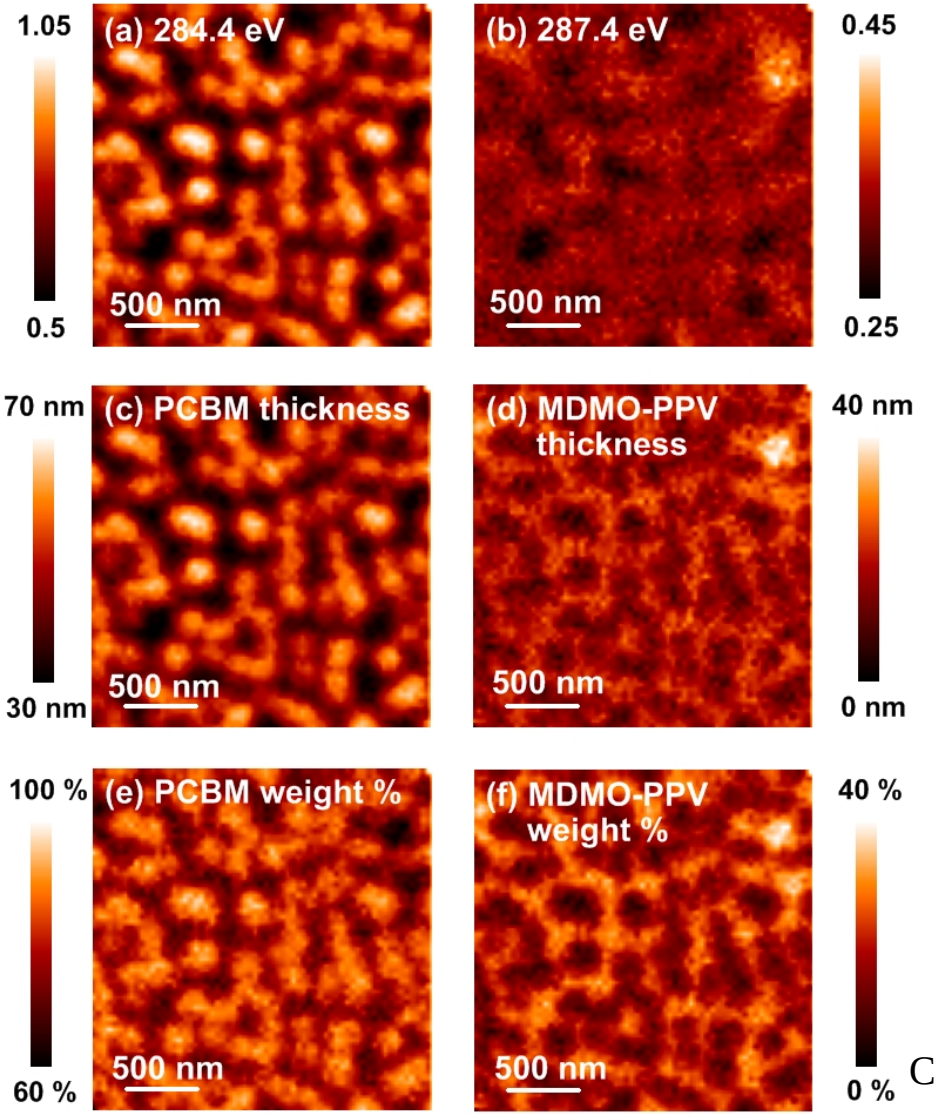
Film morphology (TEM)



Device structure
(cross section)

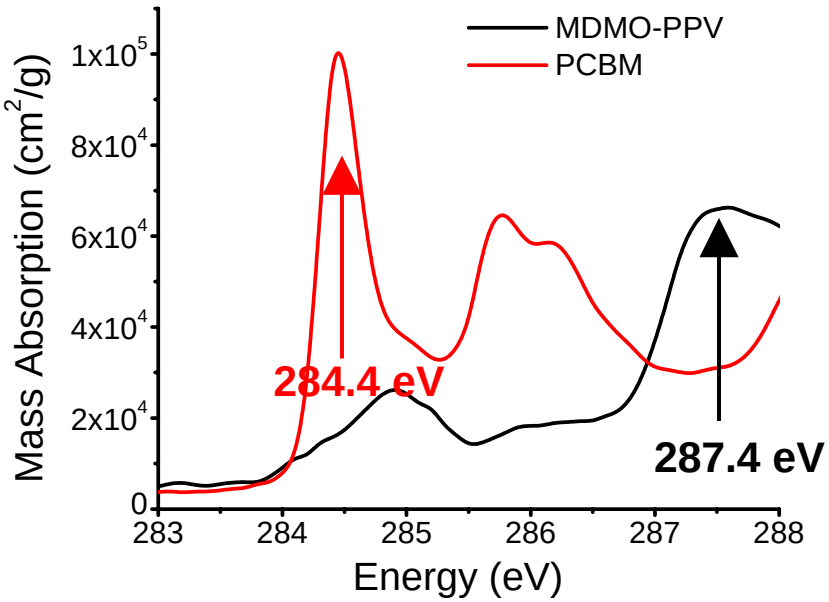
T. Martens et al. *Synth. Met.* 138, 243-247 (2003).
J. K. K van Duren, et al. *Adv. Funct. Mater.* 12, 665-669 (2002).

X-ray Microscopy of Organic Solar Cells



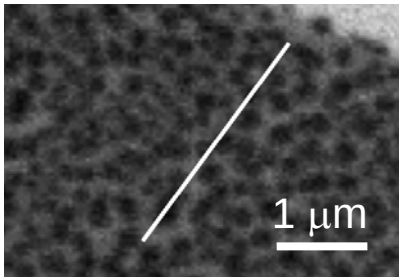
- The chemical contrast and resolution of STXM easily affords an unambiguous chemical mapping of the blended nano-morphology.

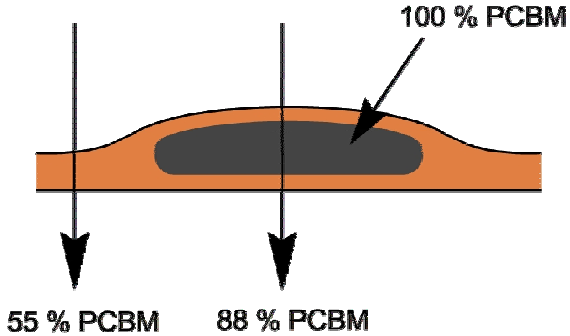
(Overall weight ratio 4 parts PCBM to 1 part MDMO-PPV)

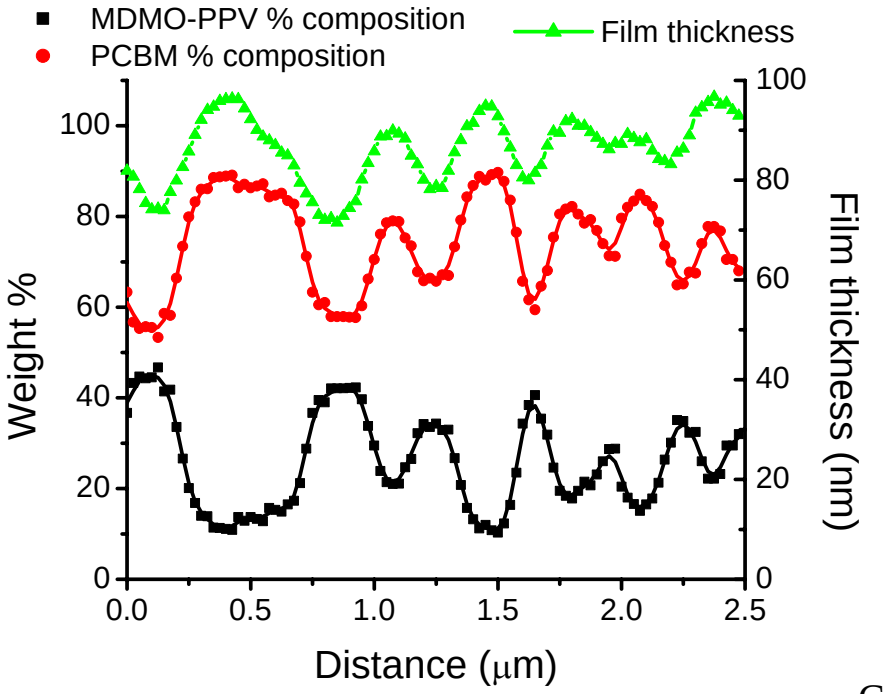


C. R. McNeill et al., *Small* **2,** 1432 - 1435 (2006).

X-ray Microscopy of Organic Solar Cells







- Quantitative analysis reveals that the "polymer-rich" phase is roughly evenly mixed, whereas the "fullerene-rich" phase is essentially pure.
- The high-purity of the fullerene-rich phase explains why these regions are poor at generating a photocurrent (see *Synth. Met.* **147** 101-104) as there are no interfaces for charge generation.

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C. R. McNeill et al., *Small* **2,** 1432 - 1435 (2006).

NC STATE

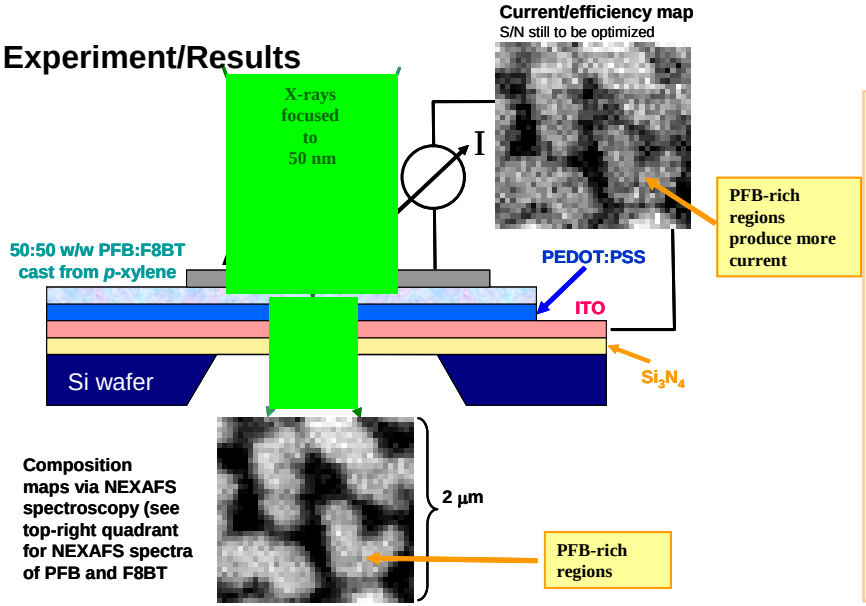
Soft X-ray Beam Induced (SoXBIC) Microscopy

B. Watts, H. Ade (NCSU), D. Queen. F. Hellman (UCB), A.L.D. Kilcoyne (ALS)

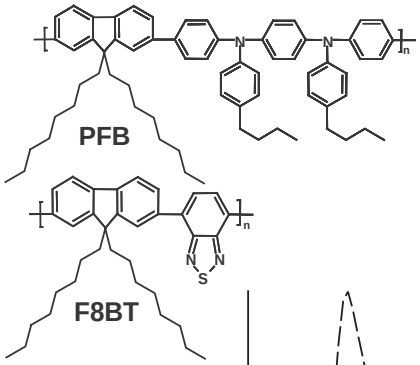
First results on Organic Photovoltaics (OPVs)
Correlation of efficiency to composition

Experiments: B. Watts, D. Queen. May 12, 2007
5.3.2 Scanning Transmission X-ray Microscope (STXM) at the ALS

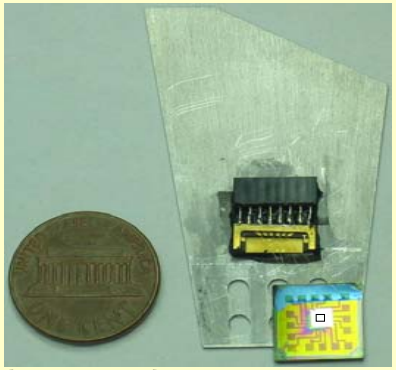
Experiment/Results

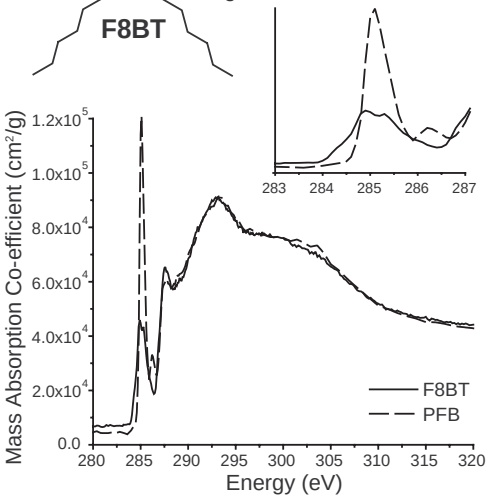


Sample prep.: Bulk heterojunction organic photovoltaic (OPV) device based on PFB and F8BT



Fully functional OPV device on STXM sample holder



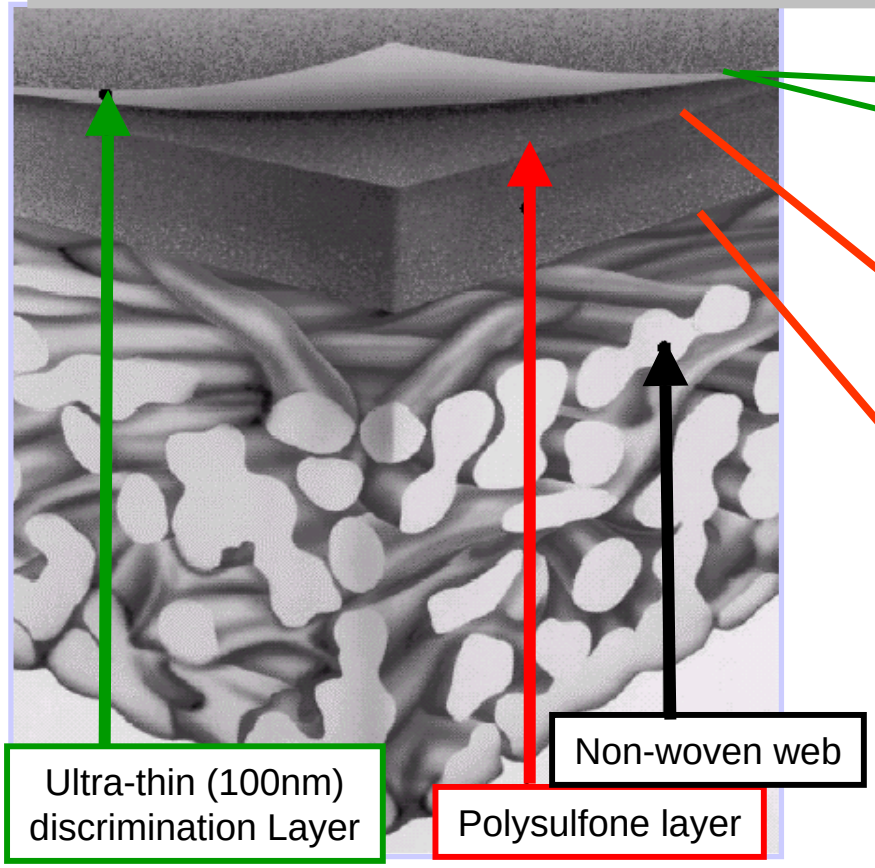


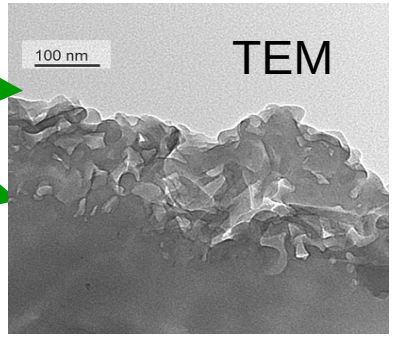
NEXAFS spectra

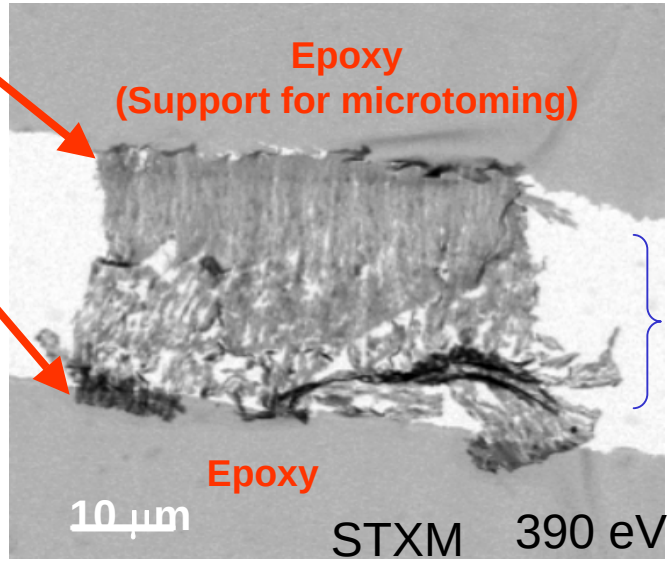
- **OPV device process control and optimization**
  - **Process** *feedback* **greatly improved by this kind of characterization**
- **Quantitative, simultaneous** *composition and efficiency* **maps**
  - **Better understanding of** *device bottlenecks,* **aids** *device optimization,* **no imaging artifacts such as coupling to topography**
- **S/N of SoXBIC can still be** *significantly improved* **- these are the very first results**
- **Potential of** *10 nm* **spatial resolution in near future (now 50 nm) - 10 nm is matched to exciton diffusion length**
- **Potential to do** *3D tomography*
  - **3D morphology is critical device parameter, to determine wetting layers**
- **Characterization of multicomponent (n>2) systems possible**

Supported by DOE grants DE-FG02-98ER45737 and DE-AC02- 05CH11231

FT30 Type Reverse Osmosis Composite Membrane Structure



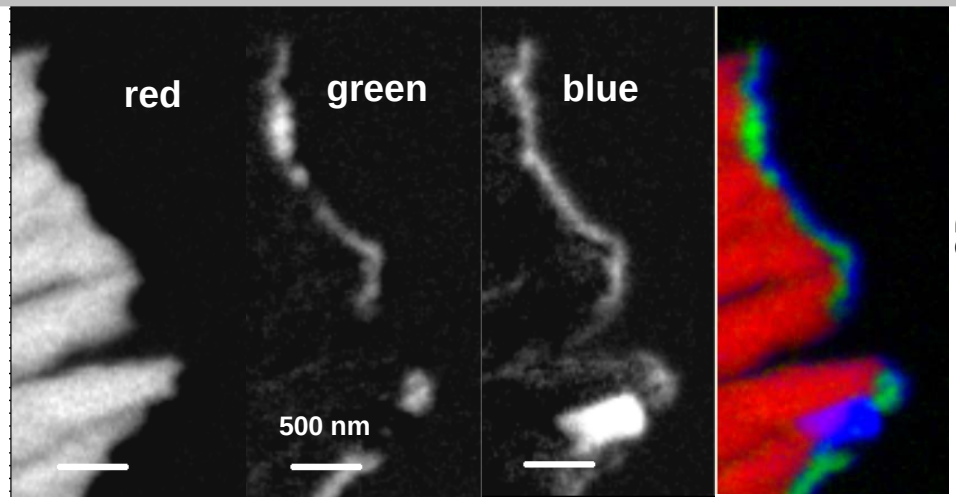


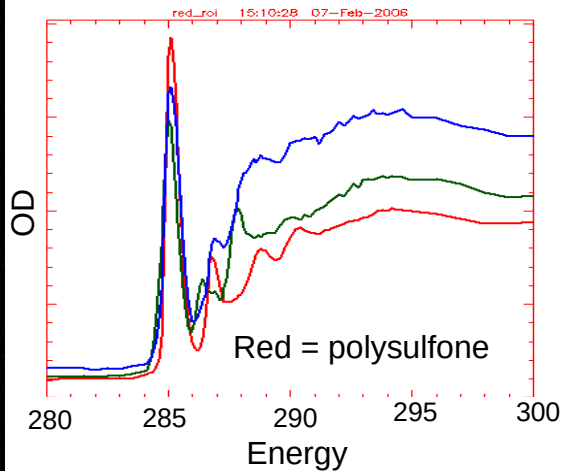


Reverse Osmosis Membranes

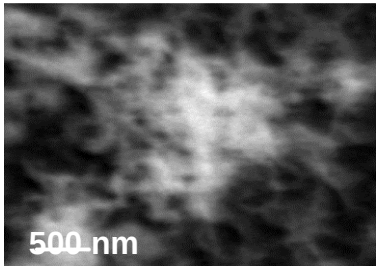
Measurements at the C K edge reveal two different phases in the polyamide layer

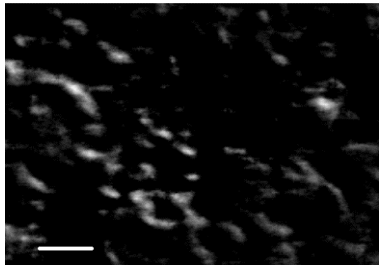
X-section

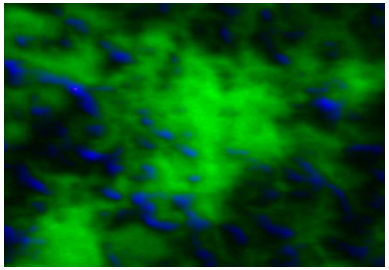




Plan view

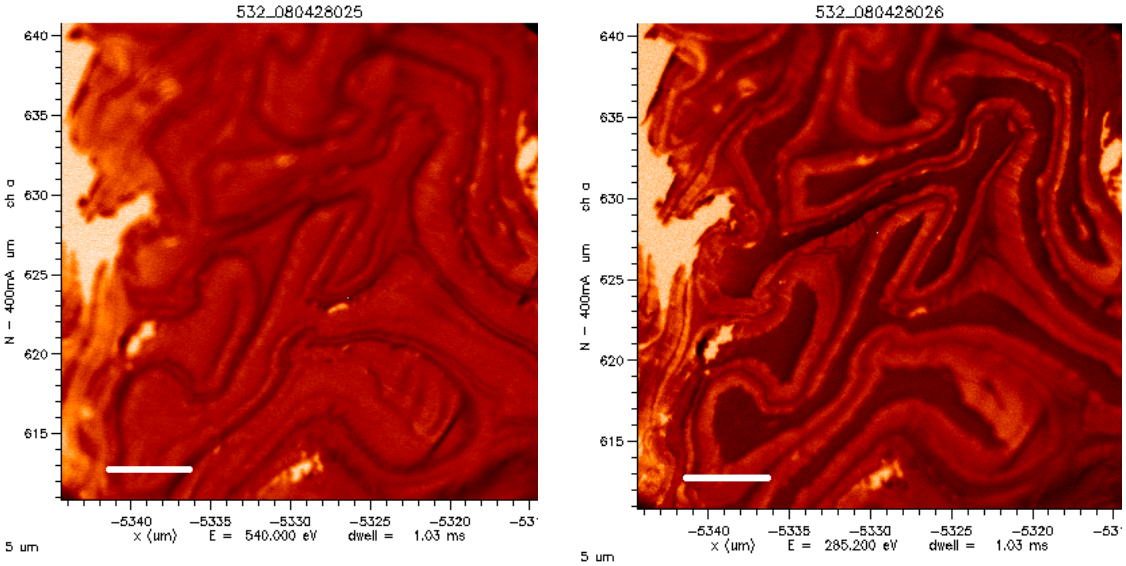




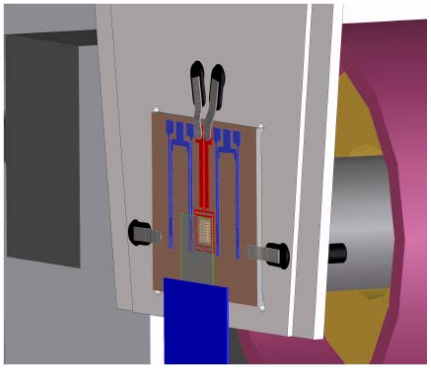


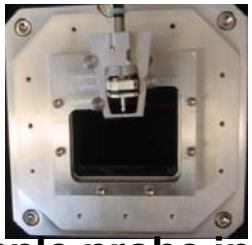
Green **Blue** **Combined false color image**

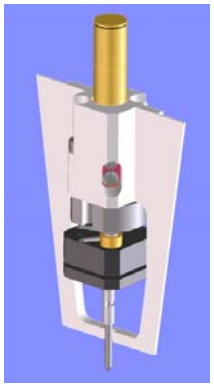
- **Composition maps calculated using spectra from cross sections**
- **Substantial phase segregation occurs laterally in the membrane**



Images of 45 M year old fossilised wood







Sample probe instrumentation

Future and current developments

STXM specific instrumentation:
Polar scans, 3D-tomography of biological samples, in-situ heating and cooling

Current energy range includes the K edge of light elements – C, N, O.

Access to the L edges of the 3d transition metal $L_{2,3}$ edges is possible but the monochromator and the STXM were not designed for this extended energy range.

An additional beam line is being planned and another dedicated microscope based on a bending magnet source to cover the energy range from 250 eV to 2000 eV is to augment the user base and the option for many new investigations relevant to the applied sciences.