

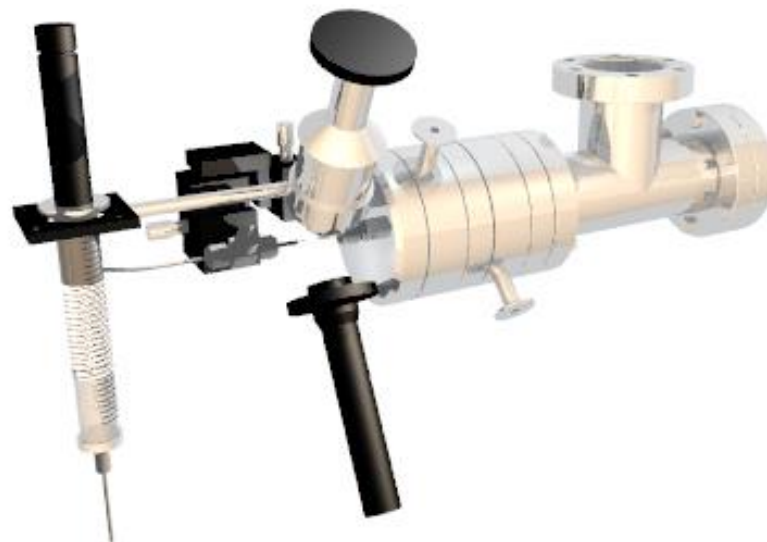


Ultra-high vacuum compatible electrospray ion beam deposition for complex, fragile molecules on surfaces

James N. O'Shea

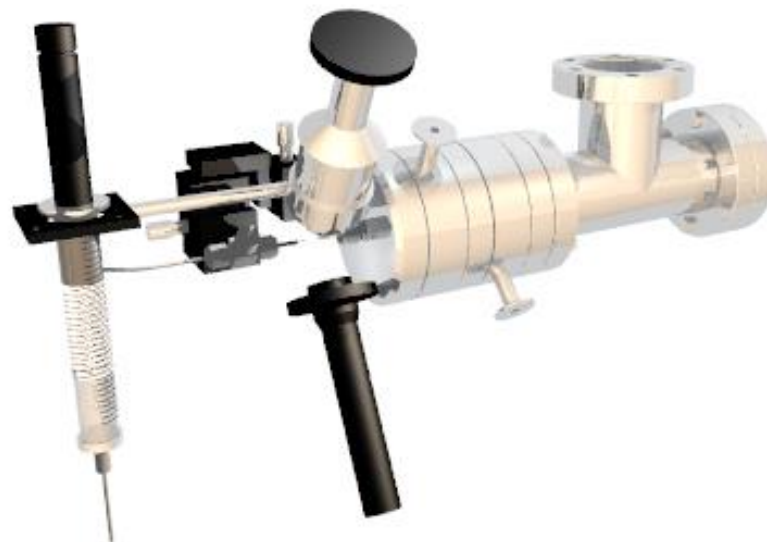
School of Physics & Astronomy, & NNC
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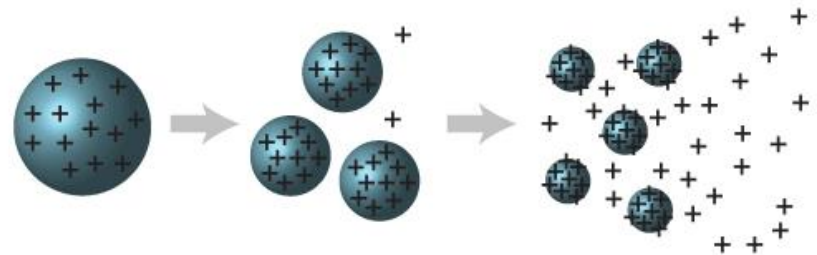
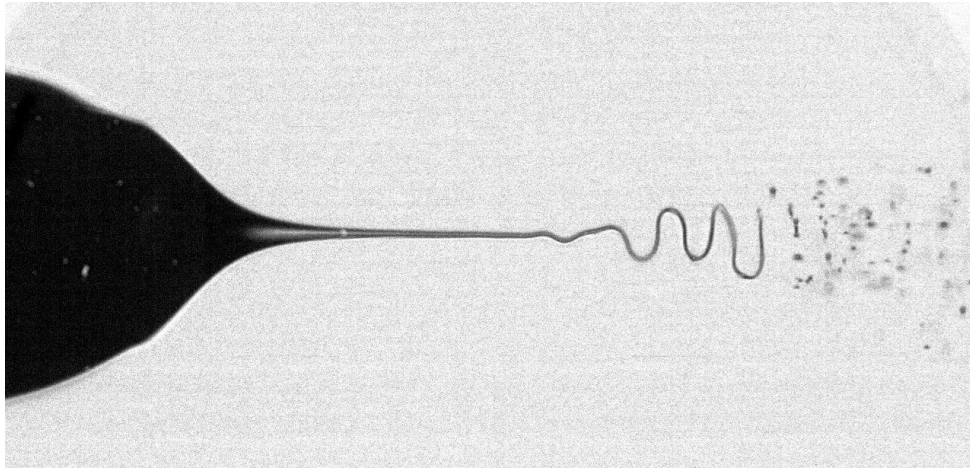




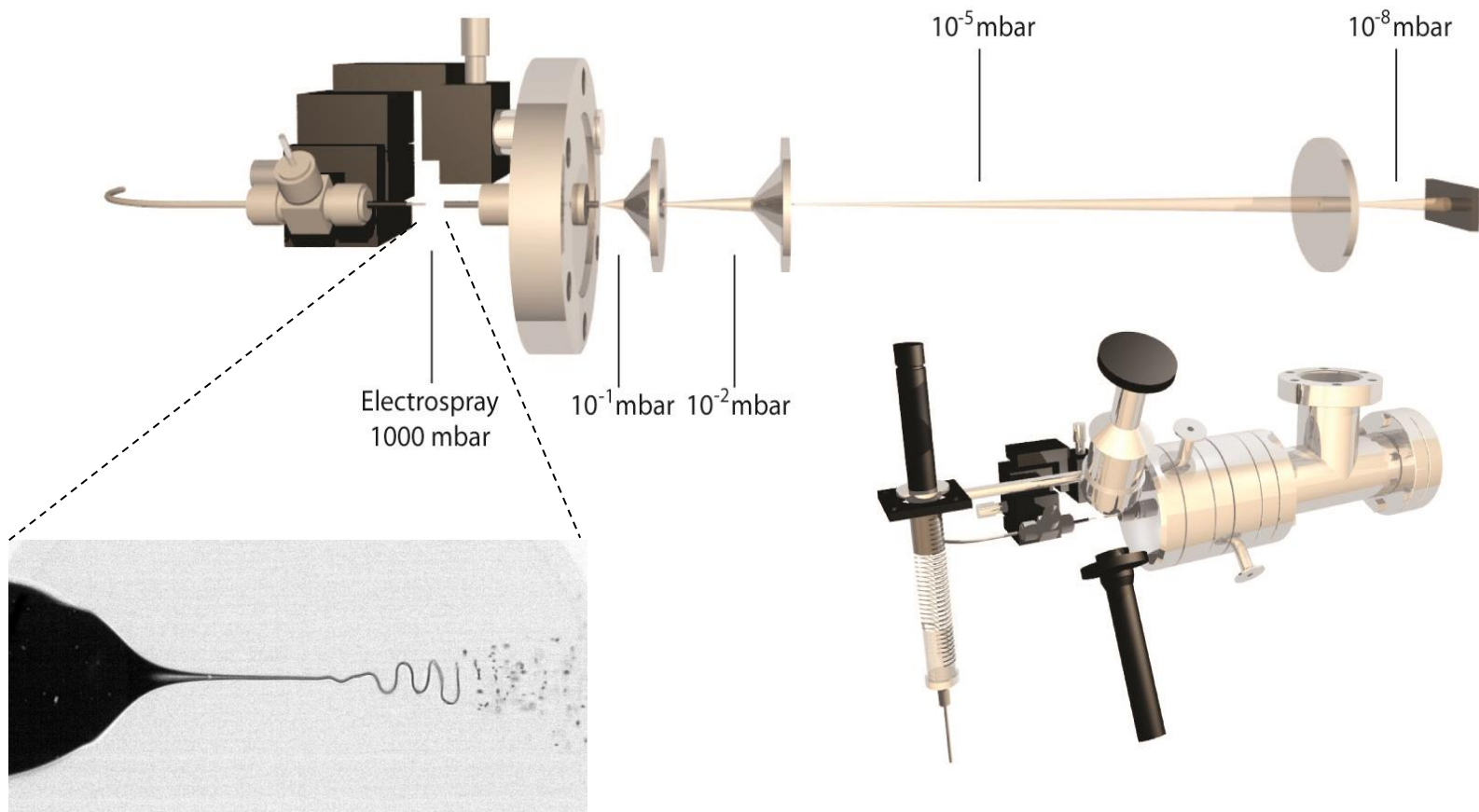
- Electrospray ionisation
- UHV Electrospray deposition sources & a new era of surface science
 - O'Shea
 - Rauschenbach & Kern



Electrospray ionisation



UHV Electrospray deposition – O'Shea



Towards individual molecules in UHV: C₆₀



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Nanotechnology 18 (2007) 455304

C J Satterley *et al*

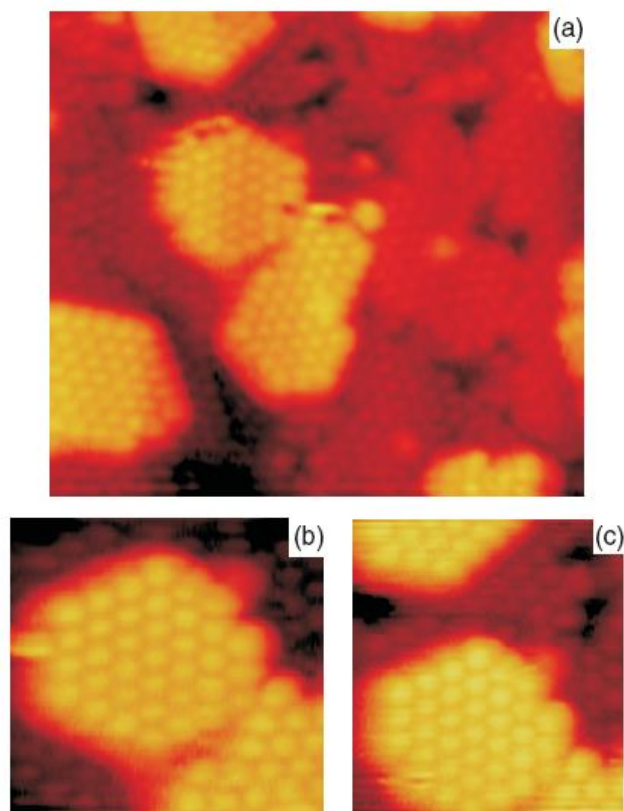


Figure 4. (a) STM image (26.4 nm × 24 nm, +2.00 V, 0.03 nA) of C₆₀ multilayers deposited by electrospray; (b) high resolution image of central region of (a) (9.7 nm × 9.2 nm, +2.00 V, 0.03 nA) showing hexagonal close-packed islands of C₆₀; (c) image (9.7 nm × 10.6 nm, +2.00 V, 0.03 nA) as (b).

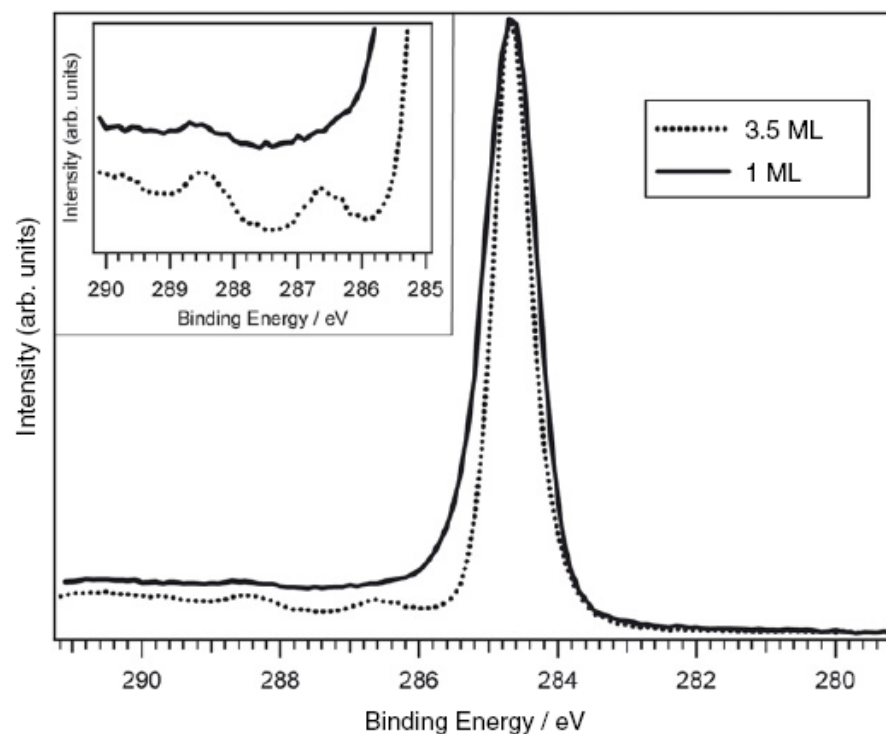
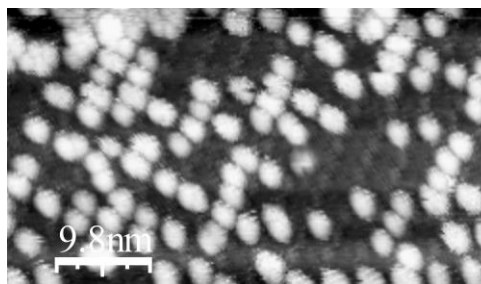
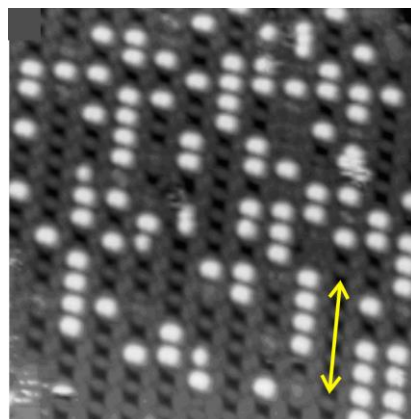
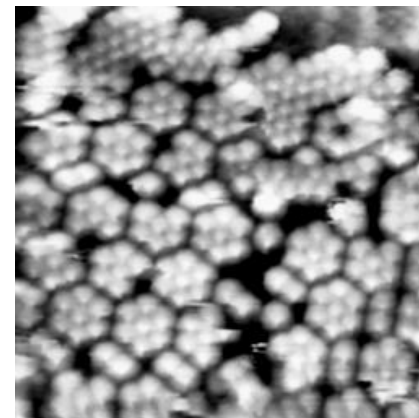
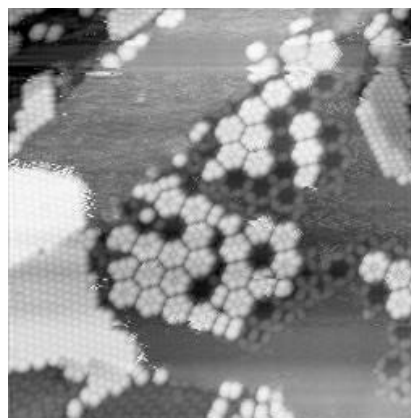
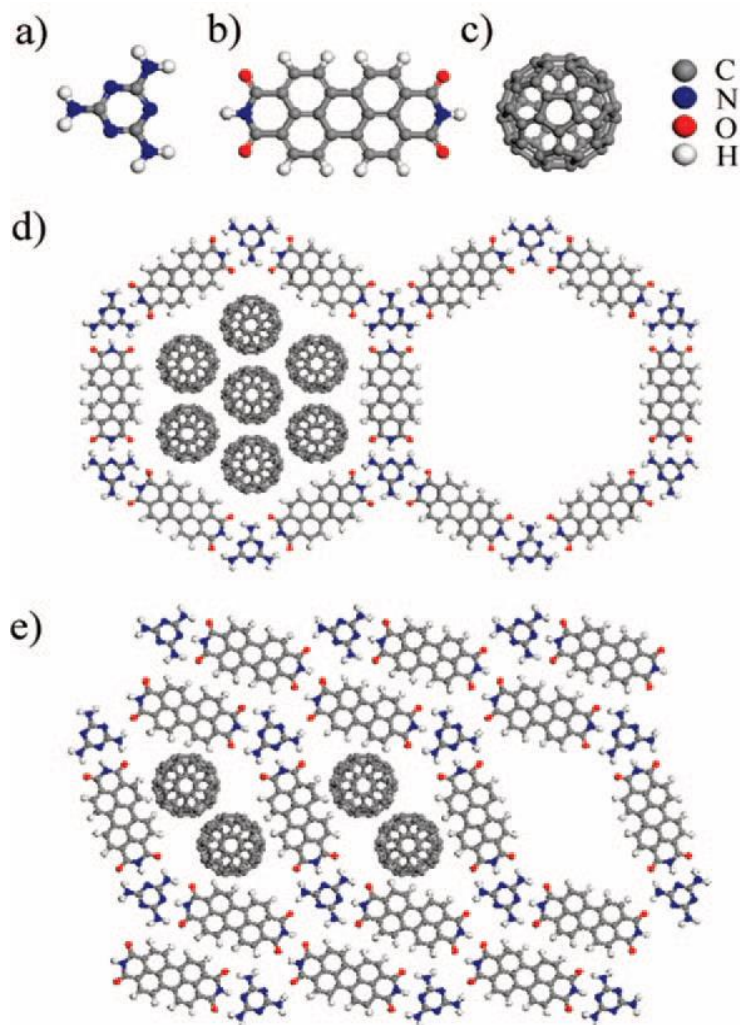


Figure 5. C 1s core level spectra for an electrosprayed monolayer and multilayer (3.5 ML) films ($h\nu = 390$ eV). Spectra have been normalized to the top of the peak and shifted on the binding energy scale for ease of comparison. The inset shows the shake-up features on the high binding energy side of the C 1s peak.

In-situ deposition of C_{60} into molecular networks



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Photoemission, resonant photoemission, and x-ray absorption of a Ru(II) complex adsorbed on rutile TiO₂(110) prepared by *in situ* electrospray deposition

Louise C. Mayor,¹ J. Ben Taylor,¹ Graziano Magnano,¹ Anna Rienzo,¹
Christopher J. Satterley,¹ James N. O'Shea,^{1,a)} and Joachim Schnadt²

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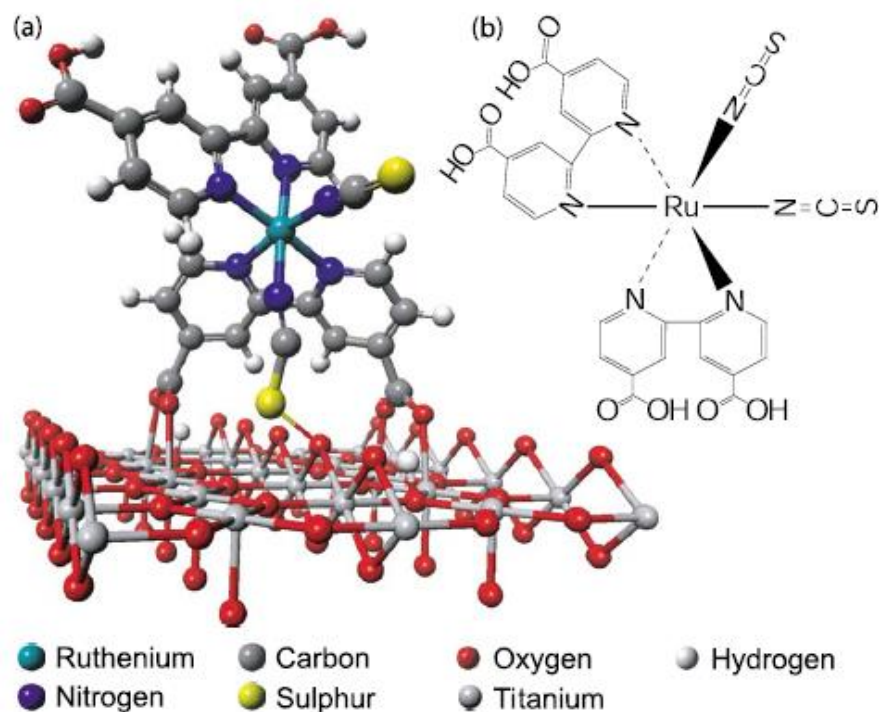
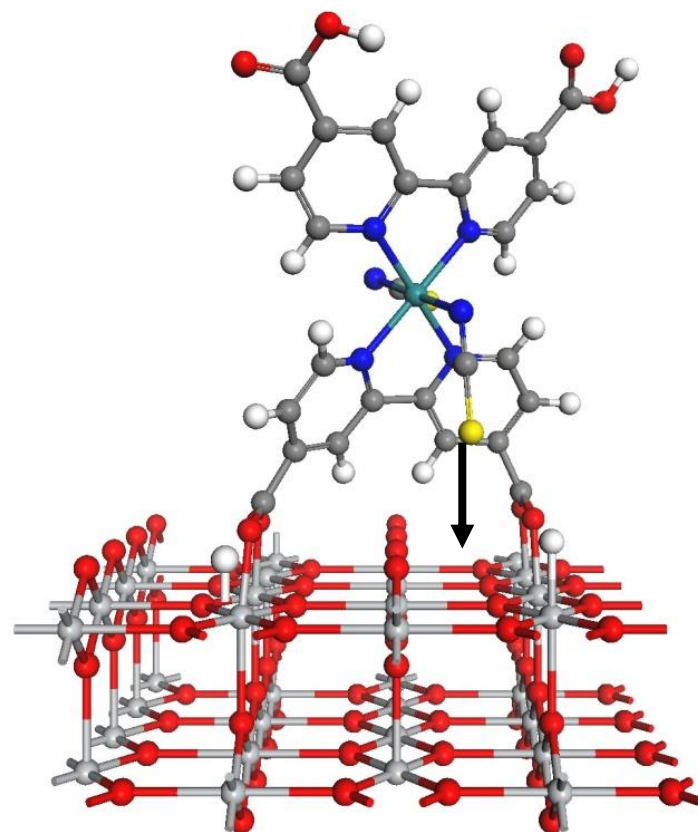
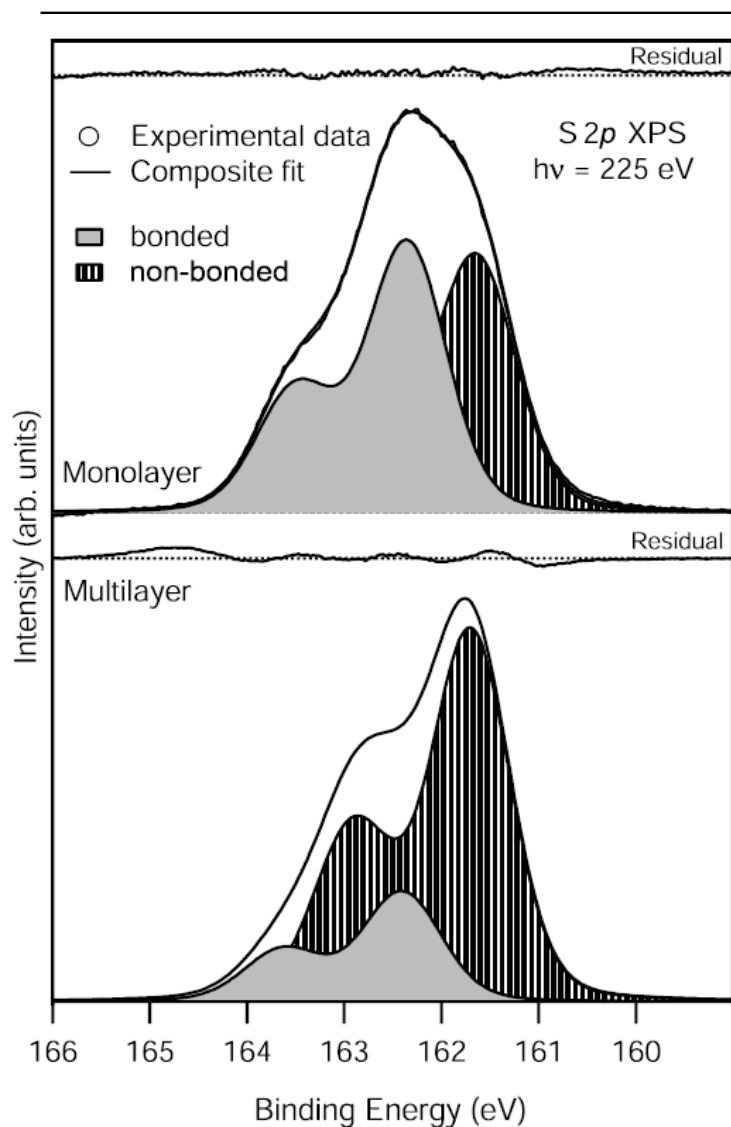


FIG. 1. (Color online) (a) N3 molecule adsorbed on TiO₂, calculated using CASTEP (Ref. 23) at the DFT-GGA level (see text for details), and (b) chemical structure of the N3 molecule.

In-situ study of N₃ on rutile TiO₂(110): XPS



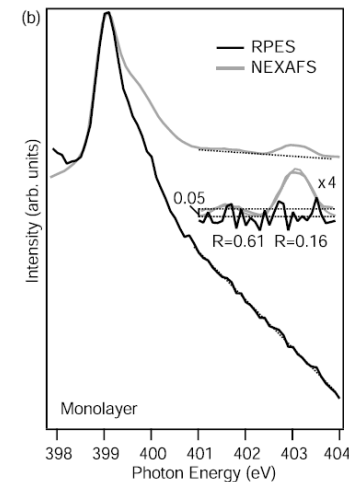
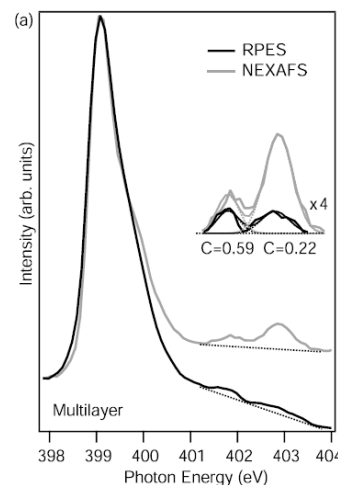
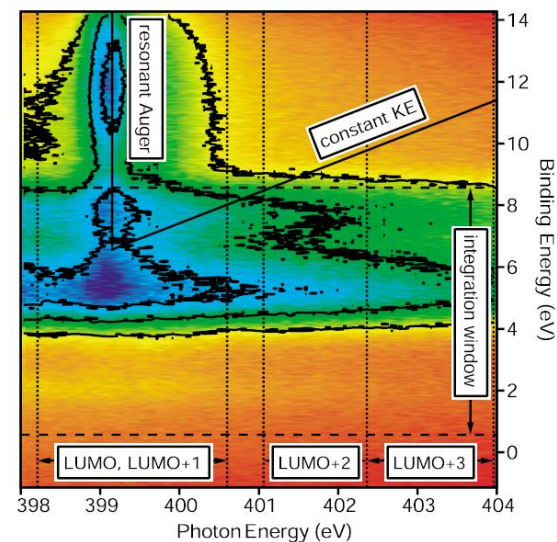
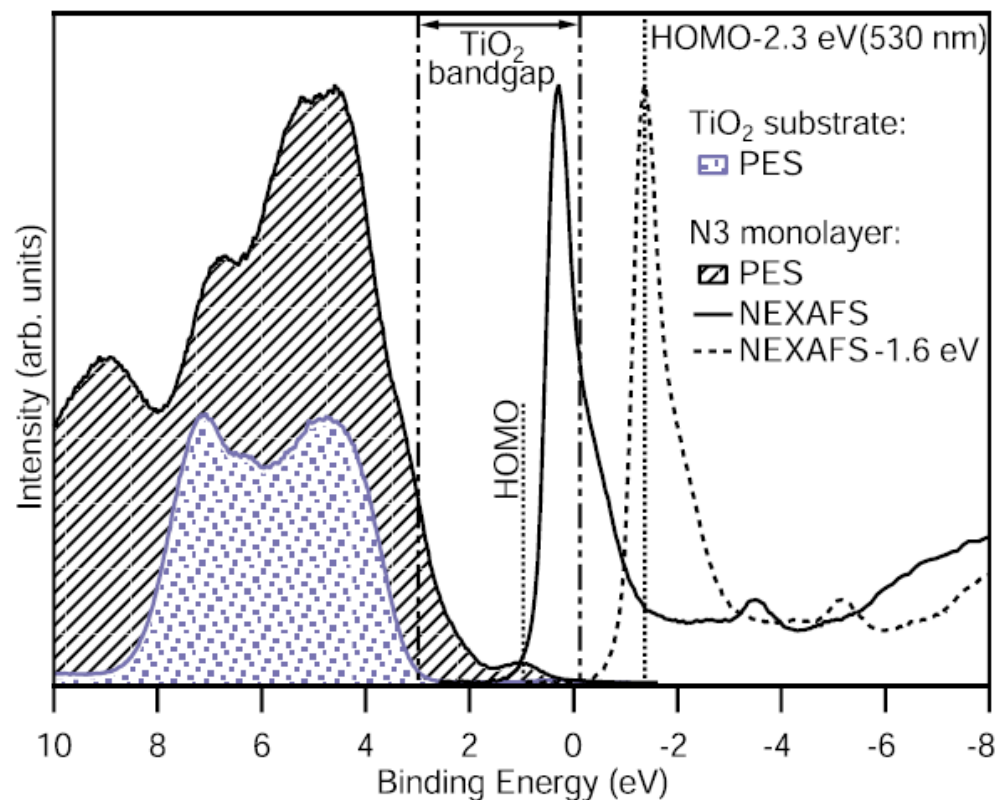
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In-situ study of N₃ on rutile TiO₂(110): PES, XAS & RPES



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L. C Mayor et al, J. Chem. Phys. **129**, 114701 (2008)

Self-assembled aggregates formed by single-molecule magnets on a gold surface



Alex Saywell¹, Graziano Magnano¹, Christopher J. Satterley¹, Luís M.A. Perdigão¹, Andrew J. Britton¹, Nassiba Taleb², María del Carmen Giménez-López², Neil R. Champness², James N. O'Shea¹ & Peter H. Beton¹

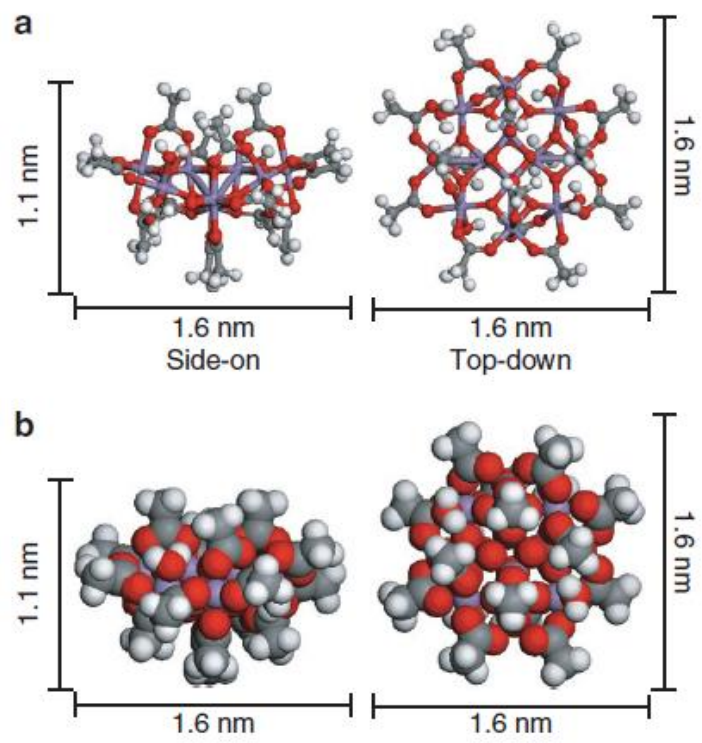
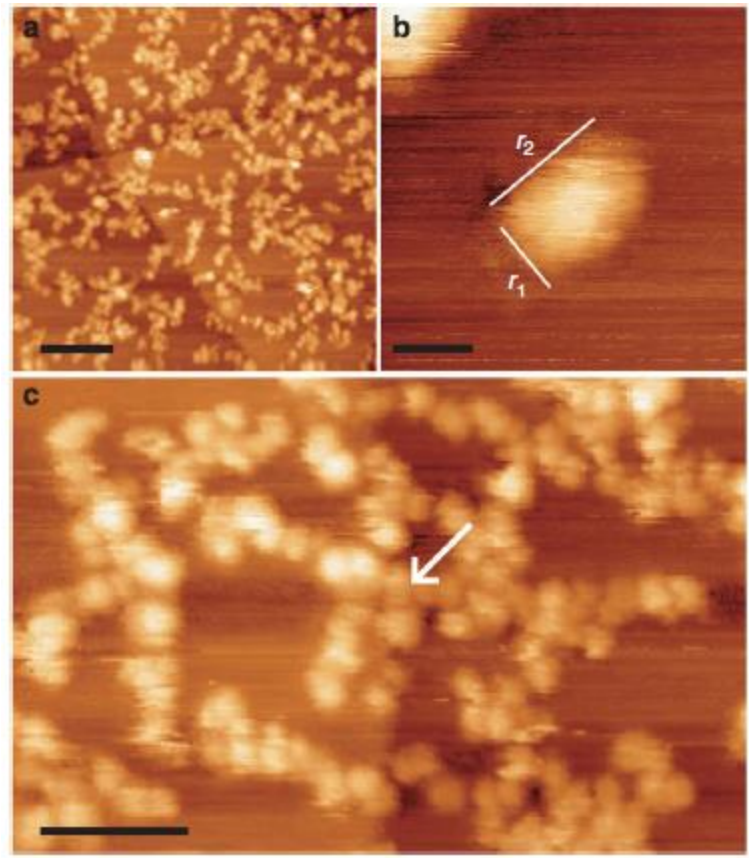


Figure 1 | Chemical structure of $\text{Mn}_{12}(\text{acetate})_{16}$. (a) $\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4$ ($\text{Mn}_{12}(\text{acetate})_{16}$), (b) structure of $\text{Mn}_{12}(\text{acetate})_{16}$ shown as a space-filling model. The dimensions of the molecule are indicated (key: grey, carbon; red, oxygen; lilac, manganese; white hydrogen).



Self-assembled aggregates formed by single-molecule magnets on a gold surface

Alex Saywell¹, Graziano Magnano¹, Christopher J. Satterley¹, Luís M.A. Perdigo¹, Andrew J. Britton¹, Nassiba Taleb², María del Carmen Giménez-López², Neil R. Champness², James N. O'Shea¹ & Peter H. Beton

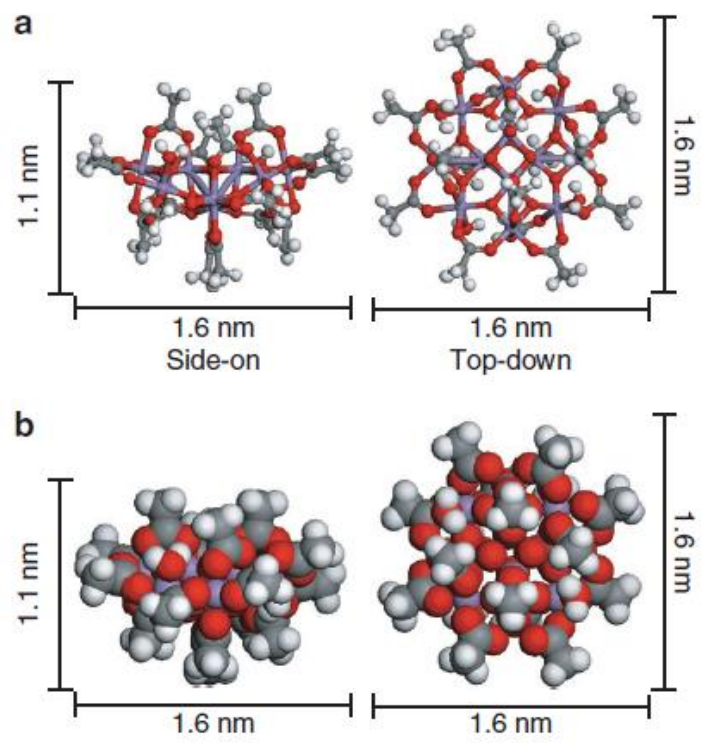


Figure 1 | Chemical structure of $\text{Mn}_{12}(\text{acetate})_{16}$. (a) $\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4$ ($\text{Mn}_{12}(\text{acetate})_{16}$), (b) structure of $\text{Mn}_{12}(\text{acetate})_{16}$ shown as a space-filling model. The dimensions of the molecule are indicated (key: grey, carbon; red, oxygen; lilac, manganese; white hydrogen).

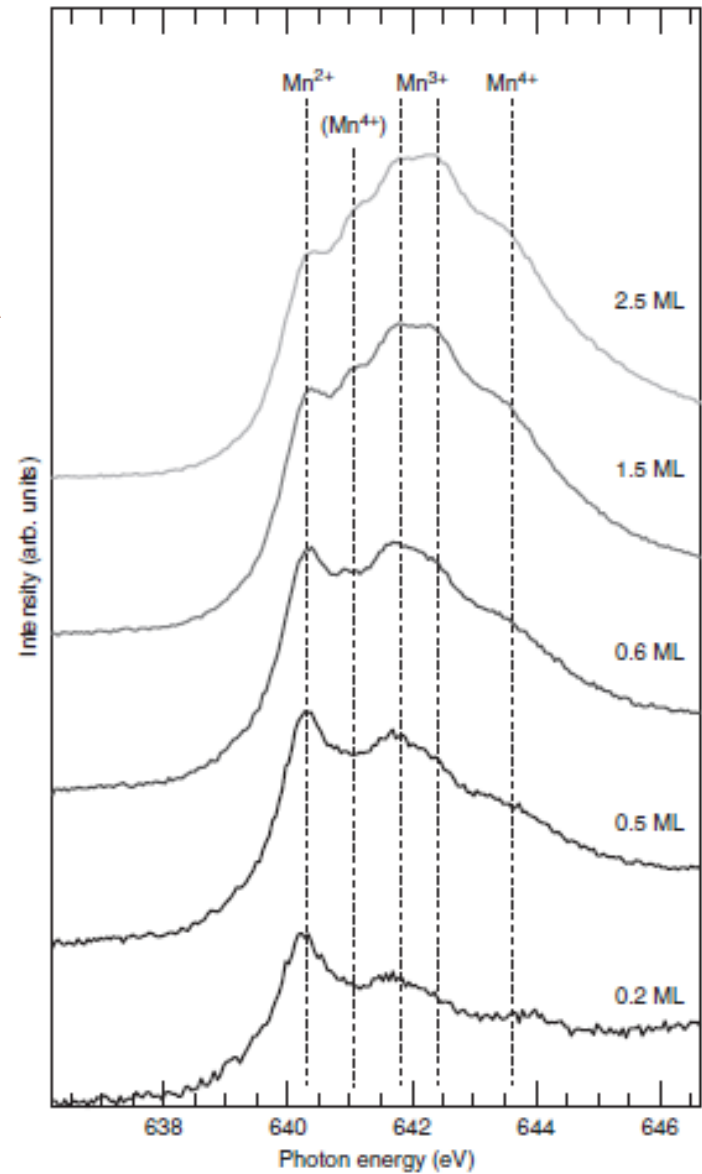
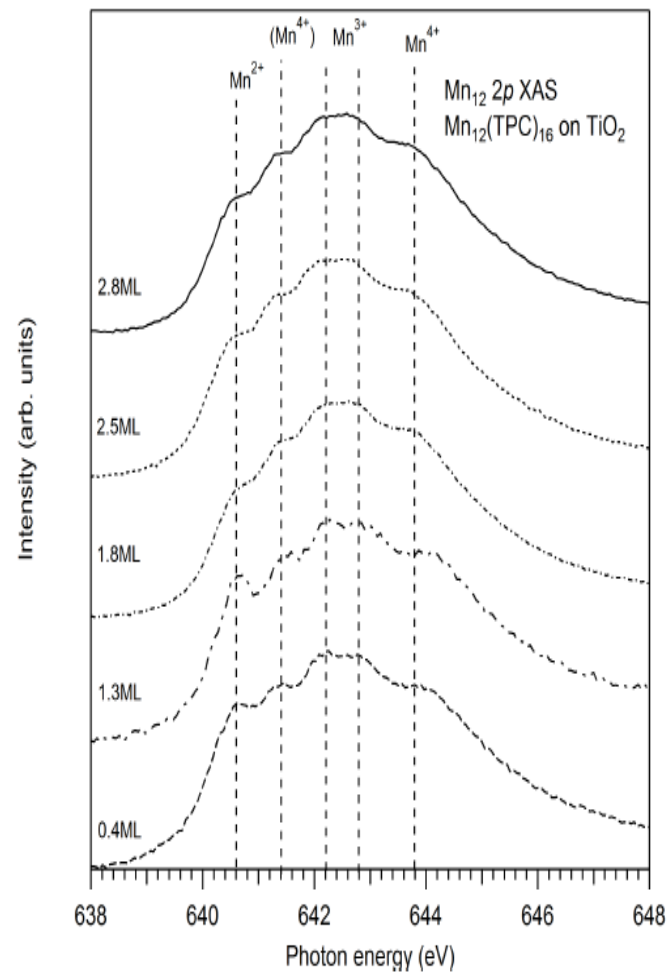
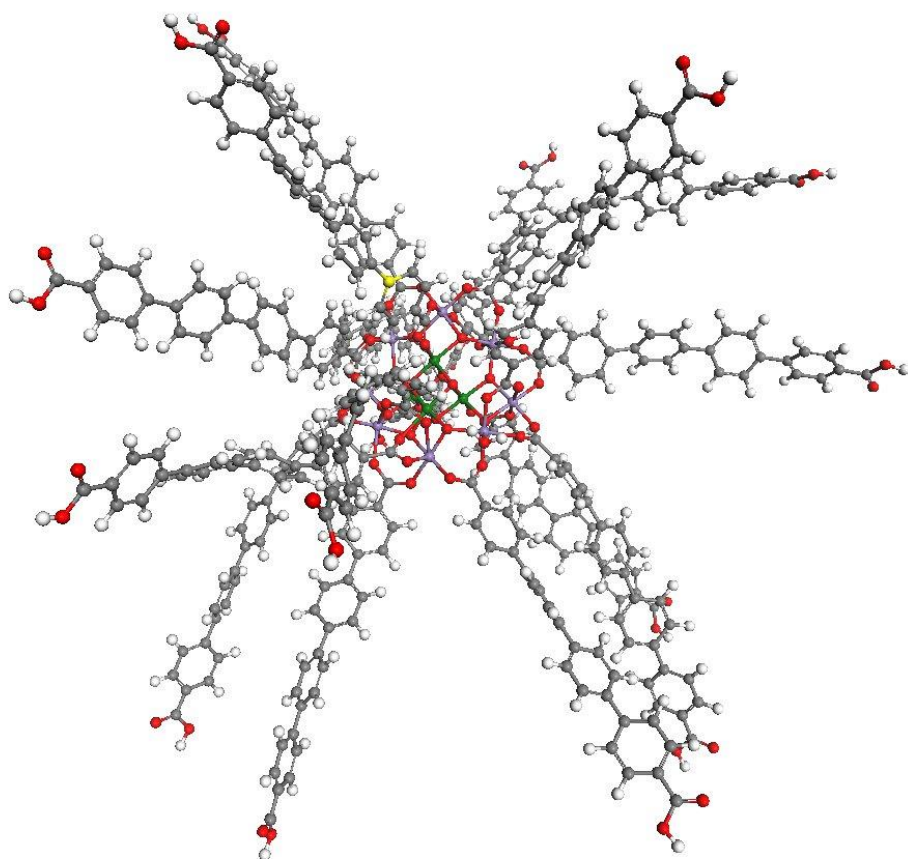


Figure 5 | NEXAFS spectra measured at the Mn 2p adsorption edge (Mn L-edge). Spectra were acquired for a range of coverages (0.2–2.5 ML (monolayer)). Photon energy was calibrated by measuring the energy separation of the Au 4f core-level photoemission peaks excited by first- and second-order X-rays. The positions of the peaks corresponding to the presence of Mn²⁺, Mn³⁺ and Mn⁴⁺ are labelled.

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K. Handrup, V. J. Richards, M. Weston, N. R. Champness and J. N. O'Shea, J. Chem. Phys. 139, 154708 (2013)

Conformation and Packing of Porphyrin Polymer Chains Deposited Using Electrospray on a Gold Surface**

Alex Saywell, Johannes K. Sprafke, Louisa J. Esdaile, Andrew J. Britton, Anna Rienzo, Harry L. Anderson, James N. O'Shea, and Peter H. Beton*

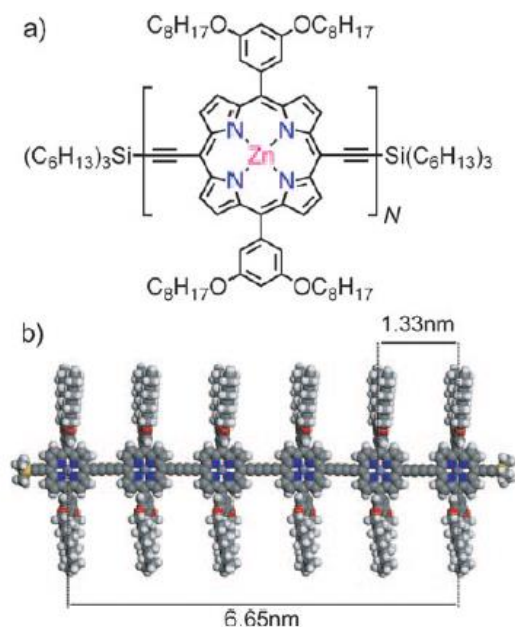
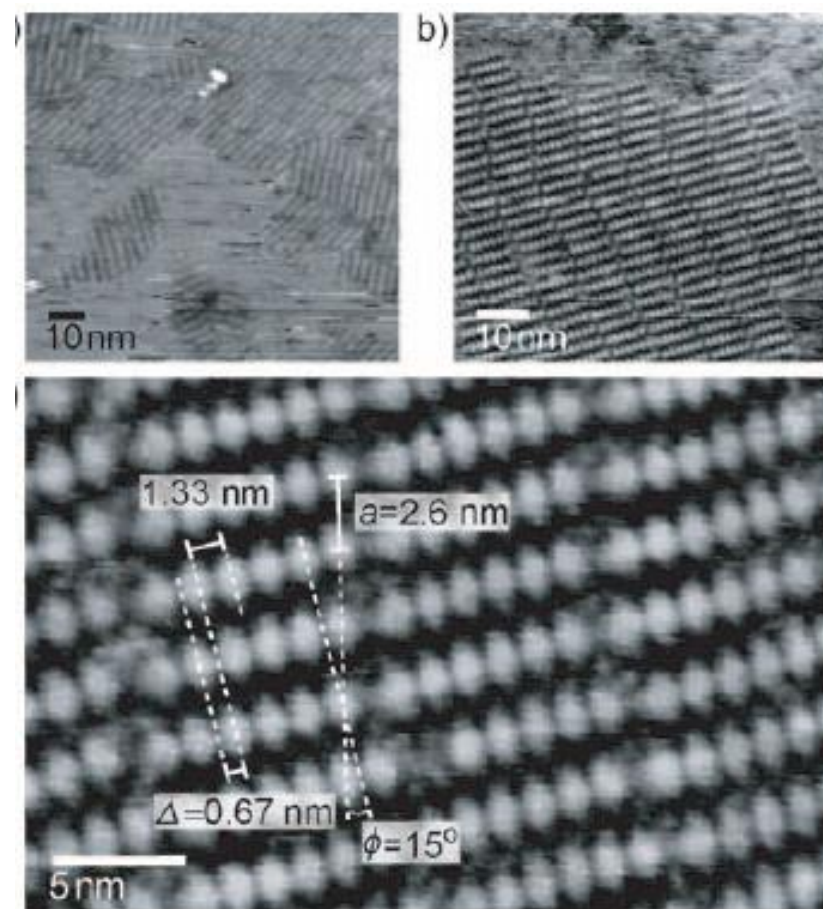


Figure 1. a) Structure of porphyrin oligomers and polymers. b) P6 molecule with the trihexylsilyl end groups truncated to trimethylsilyl groups for clarity.



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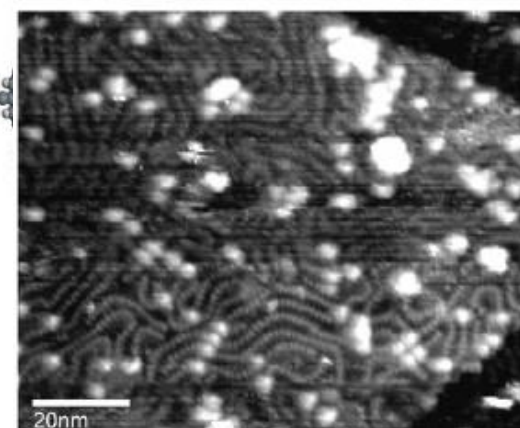
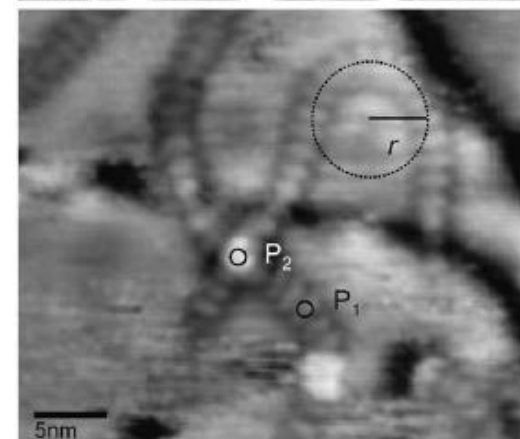
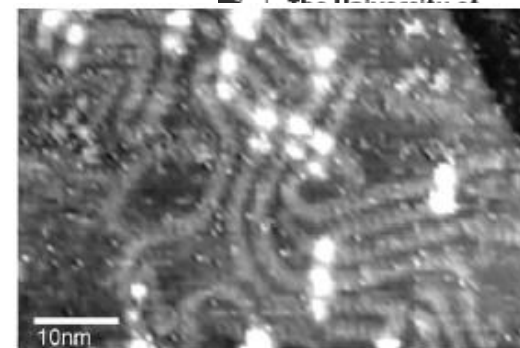
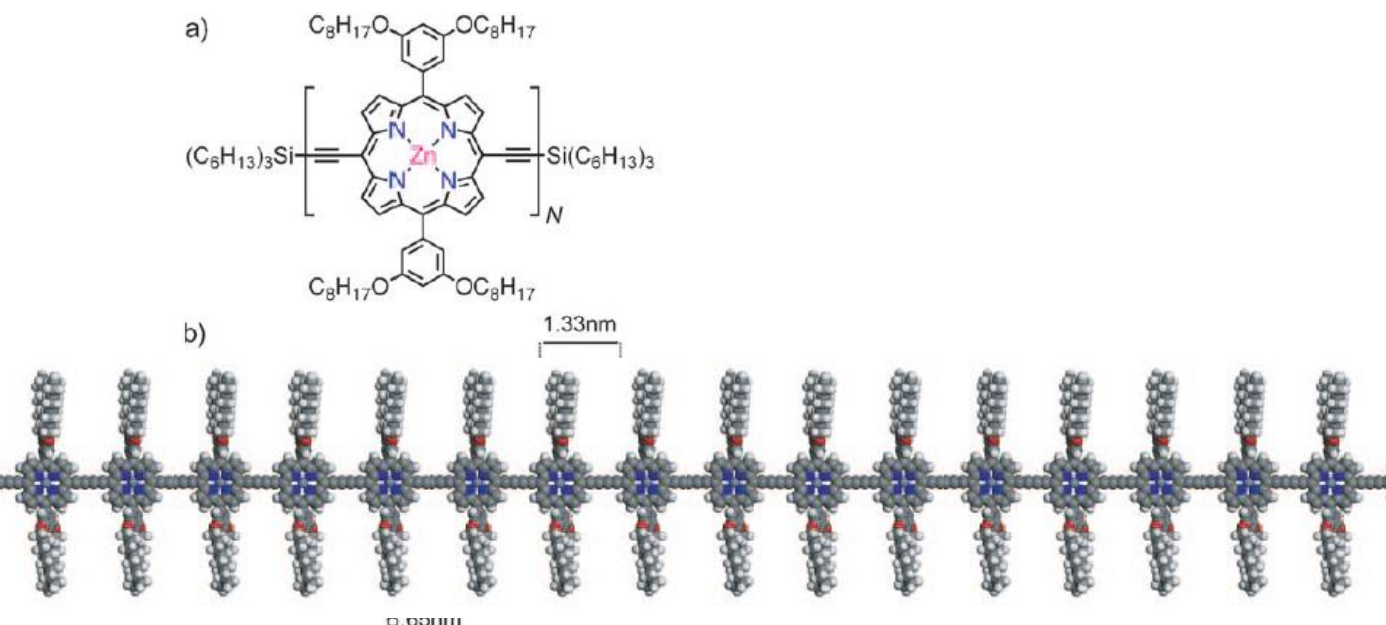
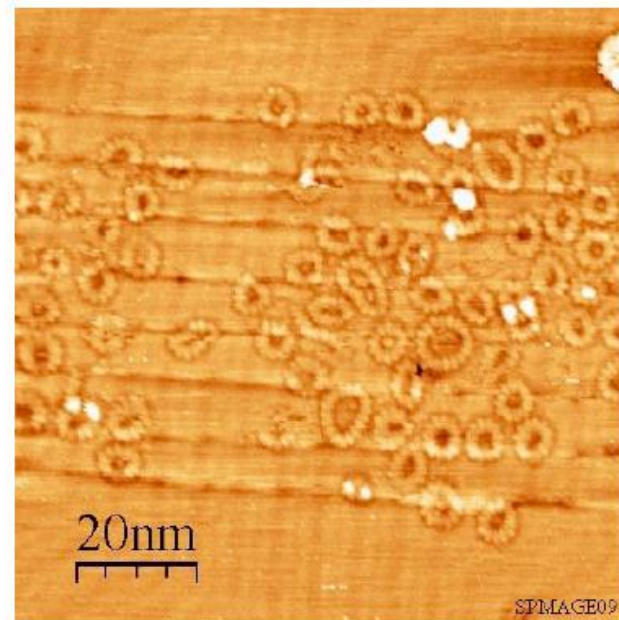
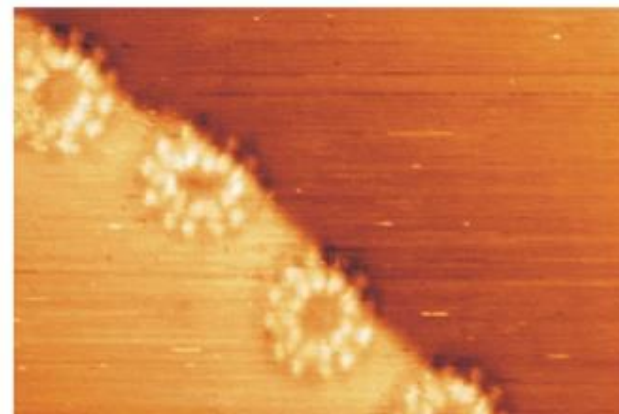
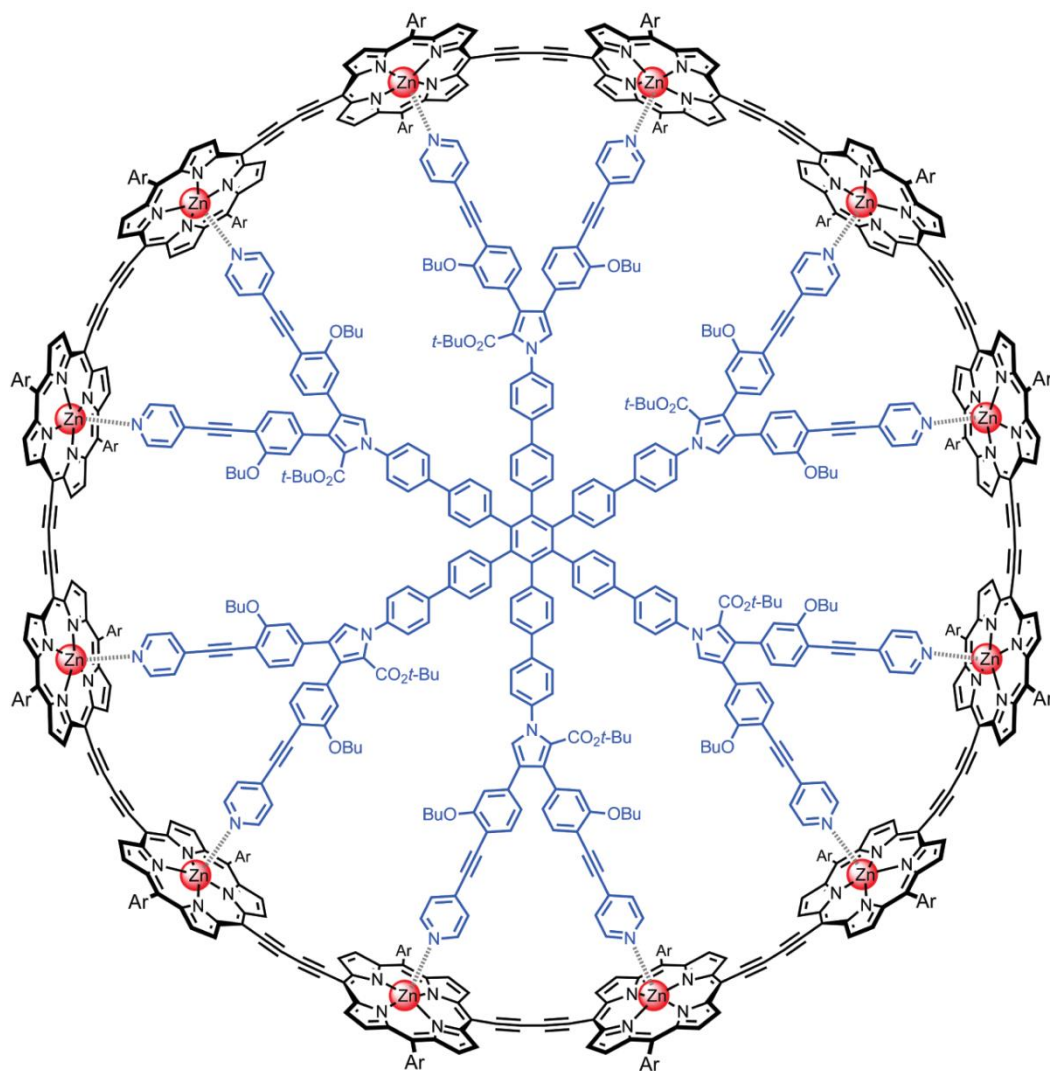


Figure 1. a) Structure of porphyrin oligomers and polymers. b) P6 molecule with the trihexylsilyl end groups truncated to trimethylsilyl groups for clarity.

Vernier templating and synthesis of a 12-porphyrin nano-ring

University of
Birmingham

Melanie C. O'Sullivan^{1*}, Johannes K. Sprafke^{1*}, Dmitry V. Kondratuk¹, Corentin Rinfray¹, Timothy D. W. Claridge¹, Alex Saywell², Matthew O. Blunt², James N. O'Shea², Peter H. Beton², Marc Malfois³ & Harry L. Anderson¹



Two Vernier-Templated Routes to a 24-Porphyrin Nanoring**

*Dmitry V. Kondratuk, Luis M. A. Perdigao, Melanie C. O'Sullivan, Simon Svatek, Gareth Smith, James N. O'Shea, Peter H. Beton and Harry L. Anderson**

Dedicated to Professor Fraser Stoddart on the occasion of his 70th birthday

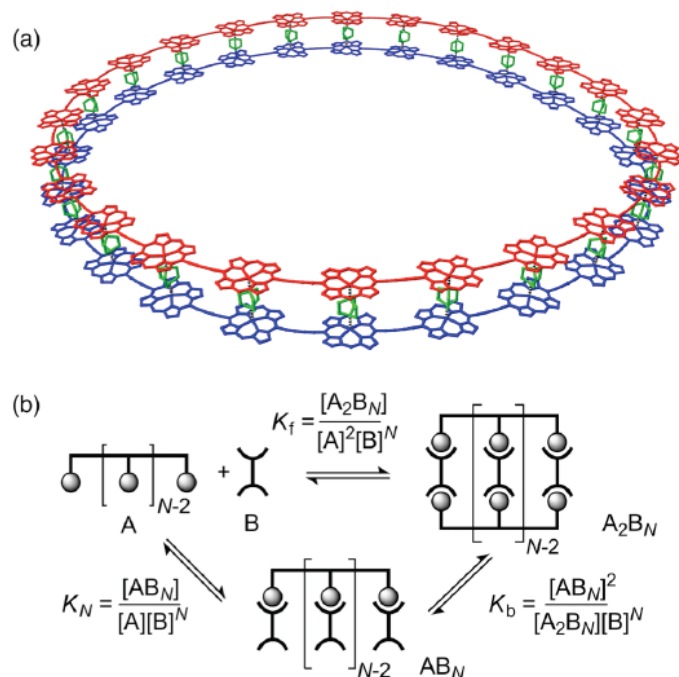


Figure 3. (a) Structure of $(\mathbf{c-P24})_2 \cdot (\text{DABCO})_{24}$ calculated using the MM+ force field (HyperChemTM). Aryl side groups and hydrogen atoms are omitted for clarity. (b) Generic thermodynamic cycle for the formation of double-strand complexes using a bidentate ligand.

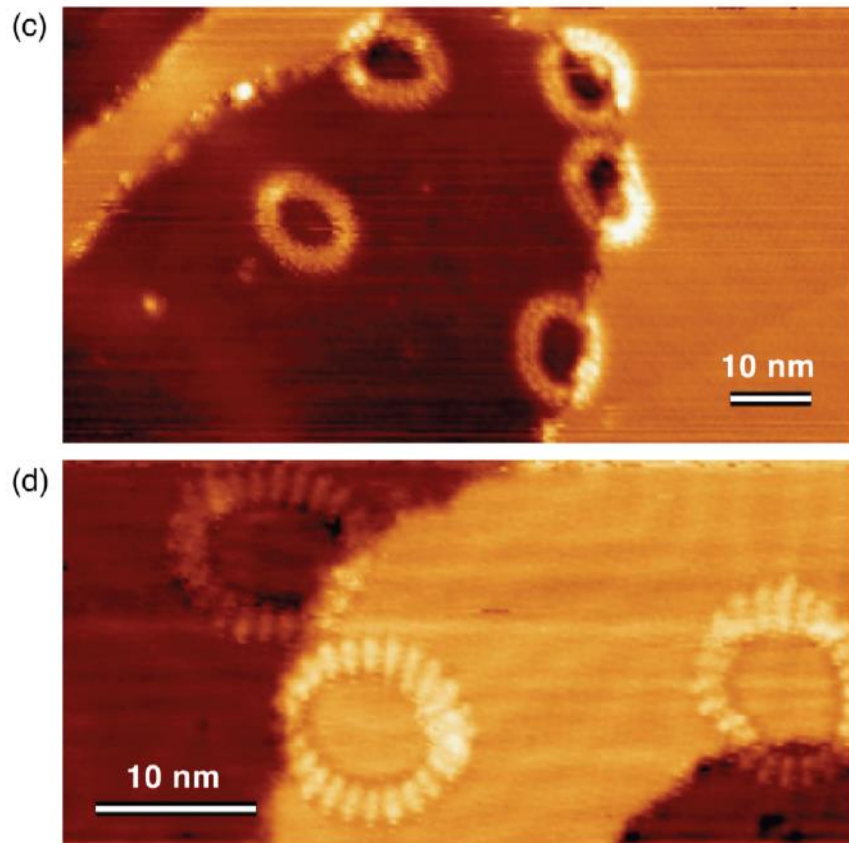
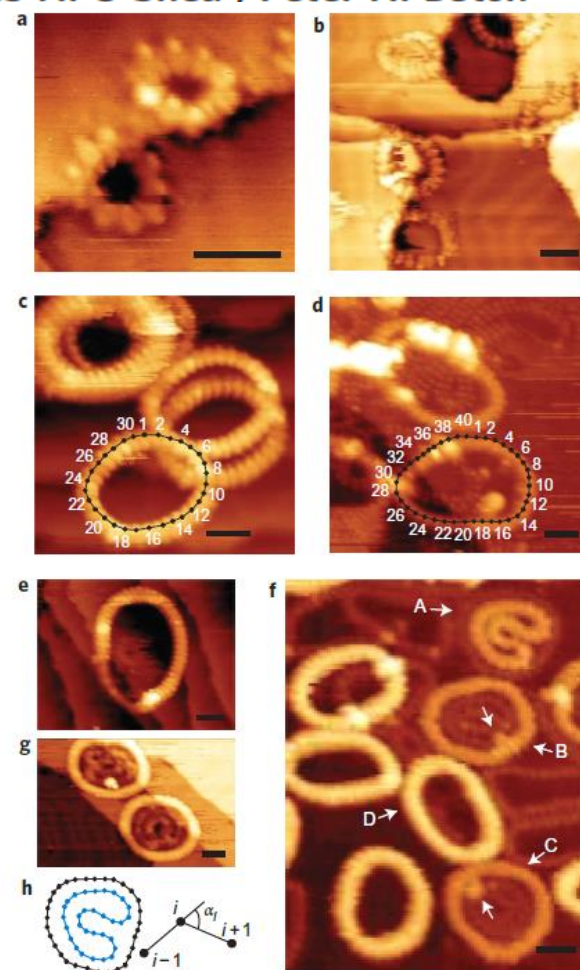


Figure 2. Characterization of the nanoring **c-P24**: (a) MALDI-ToF mass spectrum, (b), ^1H NMR spectrum (β -pyrrole protons region; $\text{CDCl}_3/1\% \text{ C}_5\text{D}_5\text{N}$, 298 K, 500 MHz) and (c,d) STM images of **c-P24** molecules on a gold surface.

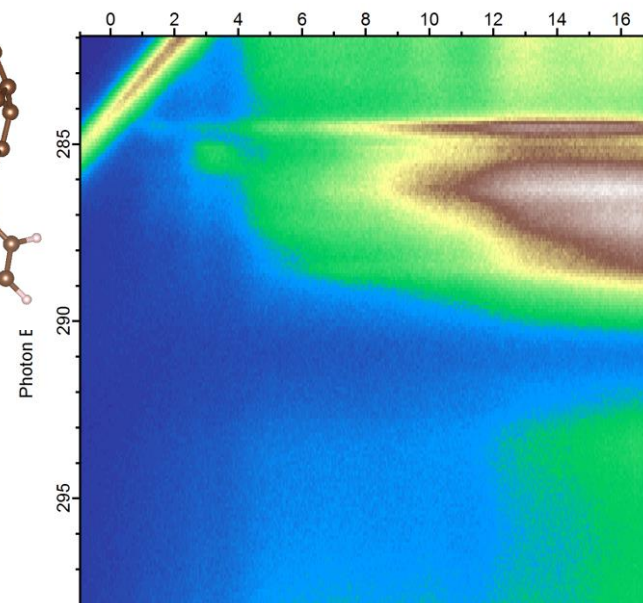
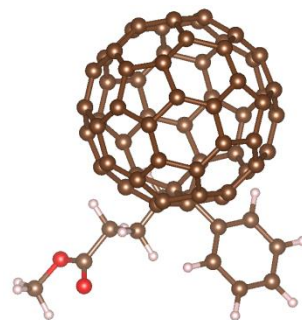
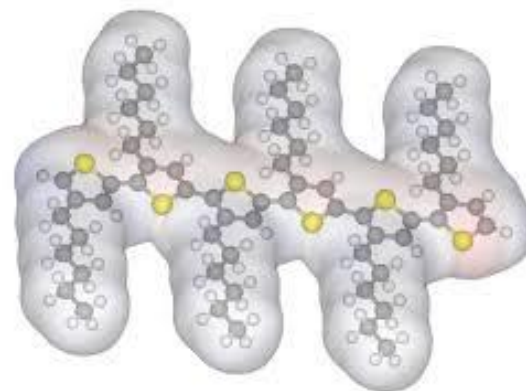
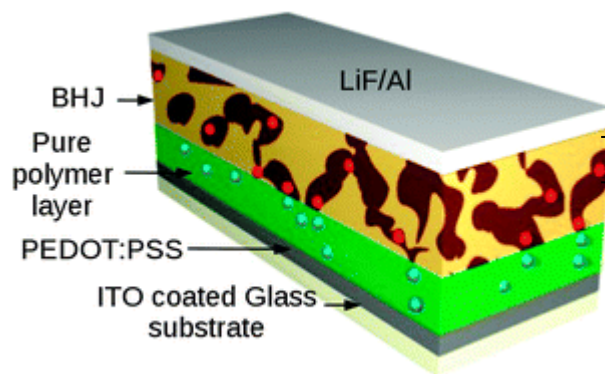
Supramolecular nesting of cyclic polymers

Dmitry V. Kondratuk¹, Luís M. A. Perdigão², Ayad M. S. Esmail², James N. O'Shea², Peter H. Beton^{2*} and Harry L. Anderson^{1*}

Figure 4 | STM images of nanorings deposited on gold surfaces under UHV. **a**, **c-P10**. **b**, **c-P20**. **c**, **c-P30**. **d**, **c-P40**. **e**, **c-P50**. **f**, Nested nanoring complexes of **c-P30**. A is a 'double-in-single' nested structure consisting of two stacked folded rings inside a single open ring. B and C are nested 'single-in-double' structures consisting of a single folded ring inside a two-layer stack of open rings. D is a triple-stack nanoring. **g**, Nested nanoring complexes of **c-P40** consisting of single-height inner rings within double-height outer rings. **h**, Schematic of nested **c-P30** structure A and definition of angle α_i . Selected rings in images **c** and **d** include numbering of subunits. Arrows in **f** identify bright features on the inner nanoring as discussed in the main text. All scale bars, 5 nm. Scanning parameters are provided in Supplementary Section E1, page 13.



Organic Solar Cells



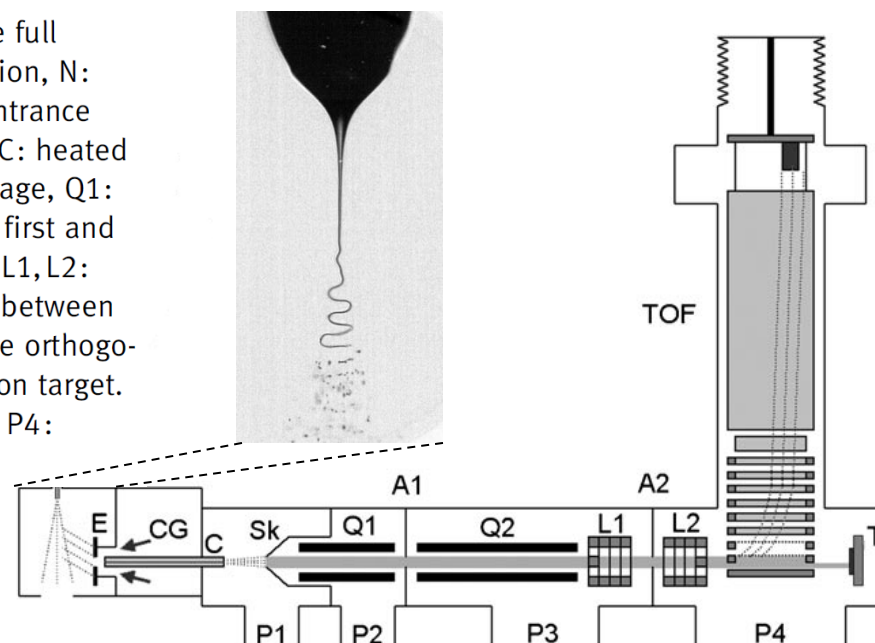
R. Temperton (2015) *Poster*

DOI: 10.1002/sml.200500479

Electrospray Ion Beam Deposition of Clusters and Biomolecules

Stephan Rauschenbach, Frank L. Stadler, Eugenio Lunedei, Nicola Malinowski, Sergej Koltsov, Giovanni Costantini, and Klaus Kern*

Figure 1. Scheme of the electrospray deposition source. The full length of the assembly is about 1 m. Sy: syringe with solution, N: spray needle, AG: assisting gas for the spray process, E: entrance plate counter electrode (−4 kV), CG: nitrogen counter gas, C: heated capillary, S: skimmer between first and second pumping stage, Q1: high-pressure quadrupole ion guide, A1: aperture between first and second ion guide, Q2: low-pressure quadrupole ion guide, L1, L2: lens system (einzel lens and steering plates), A2: aperture between third pumping stage and deposition chamber, TOF: movable orthogonal extraction time-of-flight mass spectrometer, T: deposition target. Pumping stages, P1: 1 mbar, P2: 0.1 mbar, P3: 10^{-4} mbar, P4: 10^{-6} mbar.



Deposition techniques

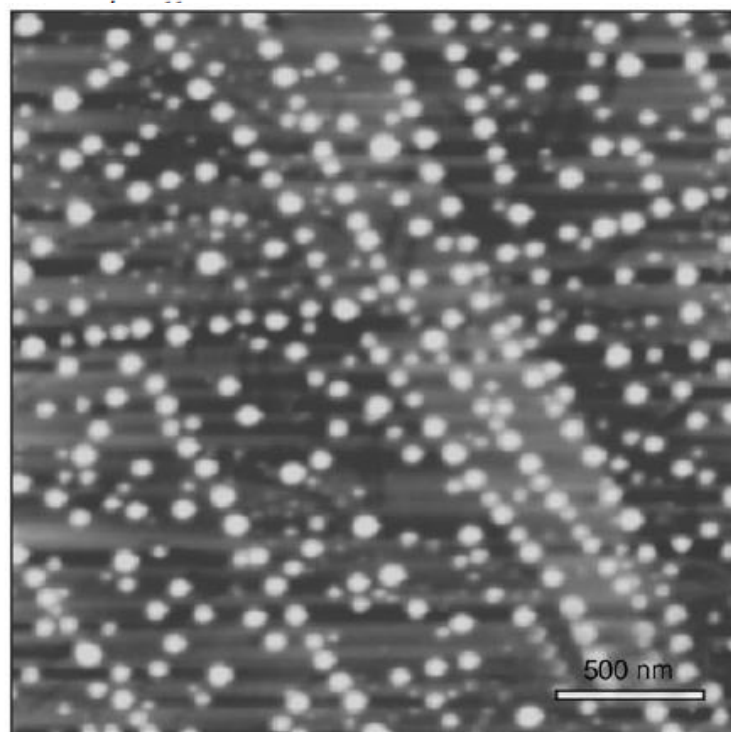


Figure 4. AFM topography of gold nanoparticles deposited in vacuum (10^{-6} mbar) on HOPG at room temperature. A current of 5 pA was used for 150 min. Large clusters with a height of 3–17 nm and a corresponding width of 250–640 nm decorate the step edges in particular.

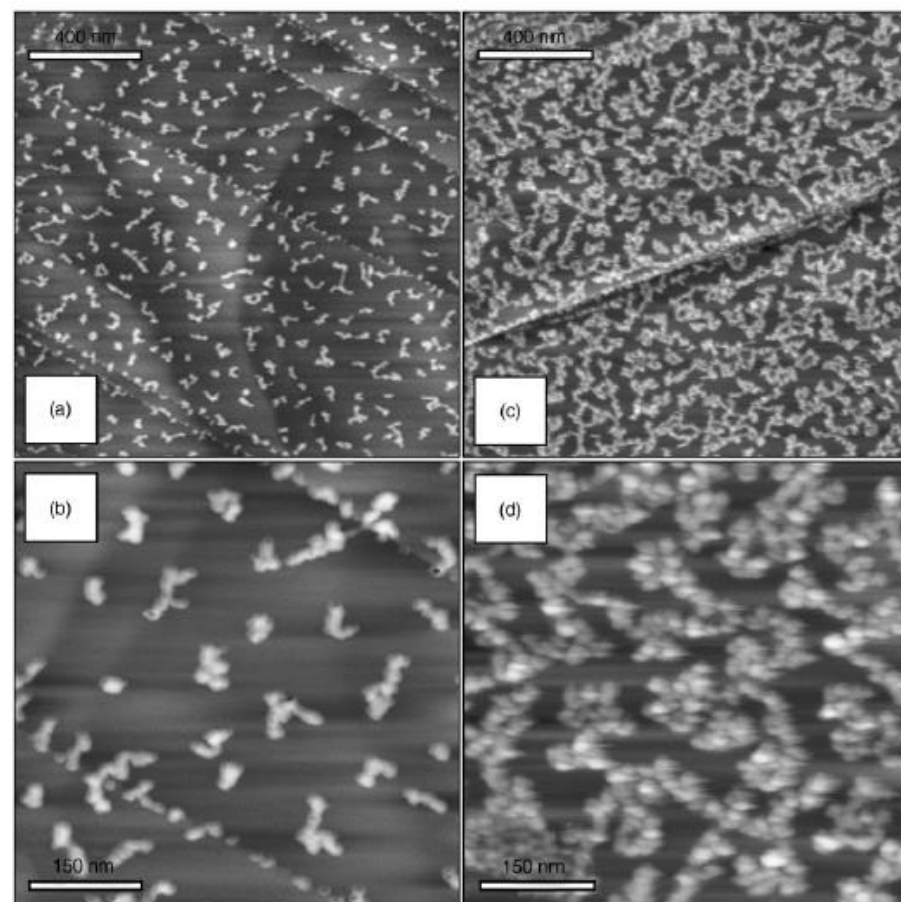


Figure 6. AFM topography of BSA deposited on HOPG under vacuum (10^{-6} mbar) at room temperature. An ion current of 30 pA was used for 85 min. Fractal aggregations formed by stringlike particles are found on the surface, indicating diffusion-limited aggregation. The spatial gradient of the beam intensity results in low (a,b) and high coverage (c,d) regions, which are close to the sample border and center, respectively.

A Close Look at Proteins: Submolecular Resolution of Two- and Three-Dimensionally Folded Cytochrome c at Surfaces

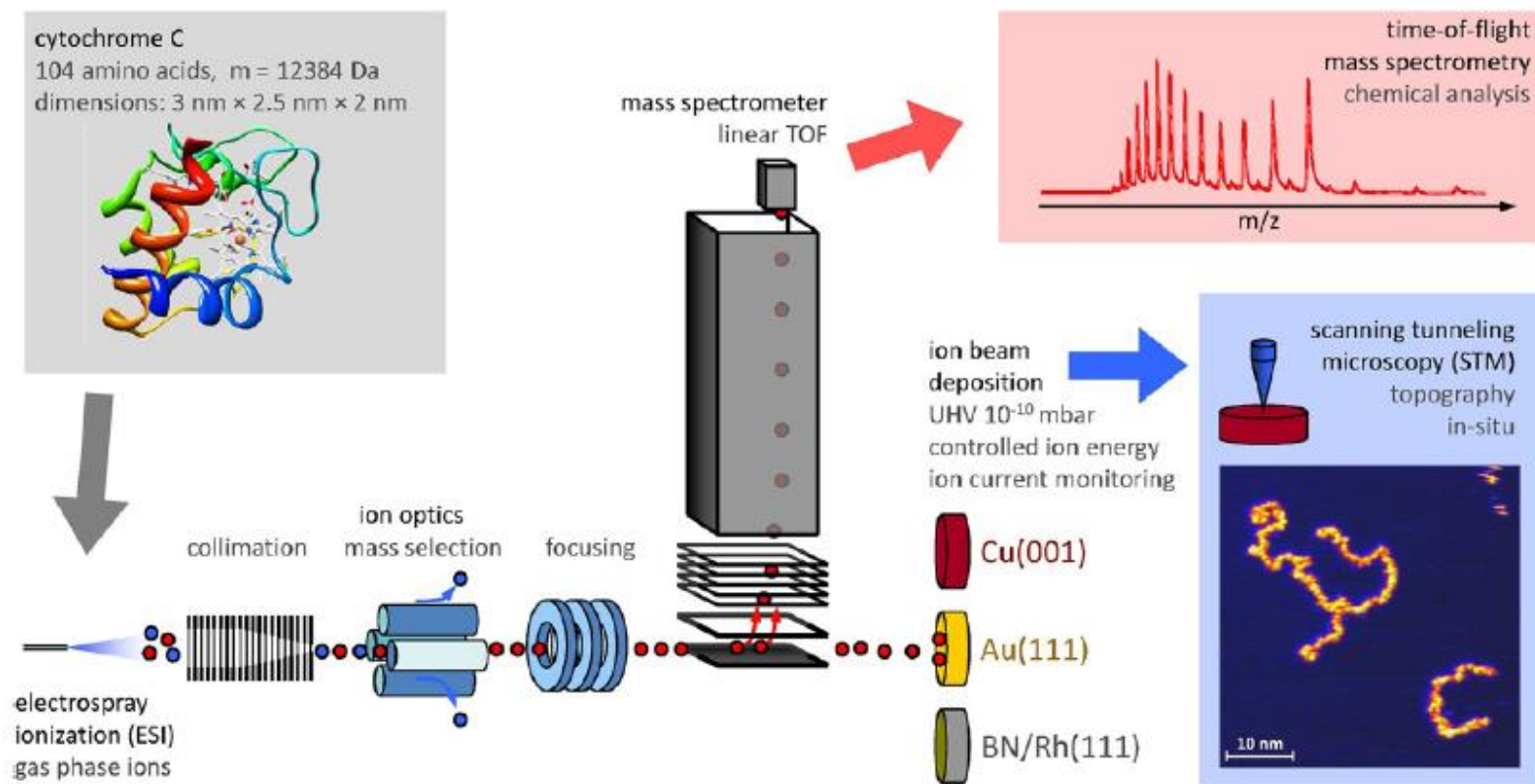
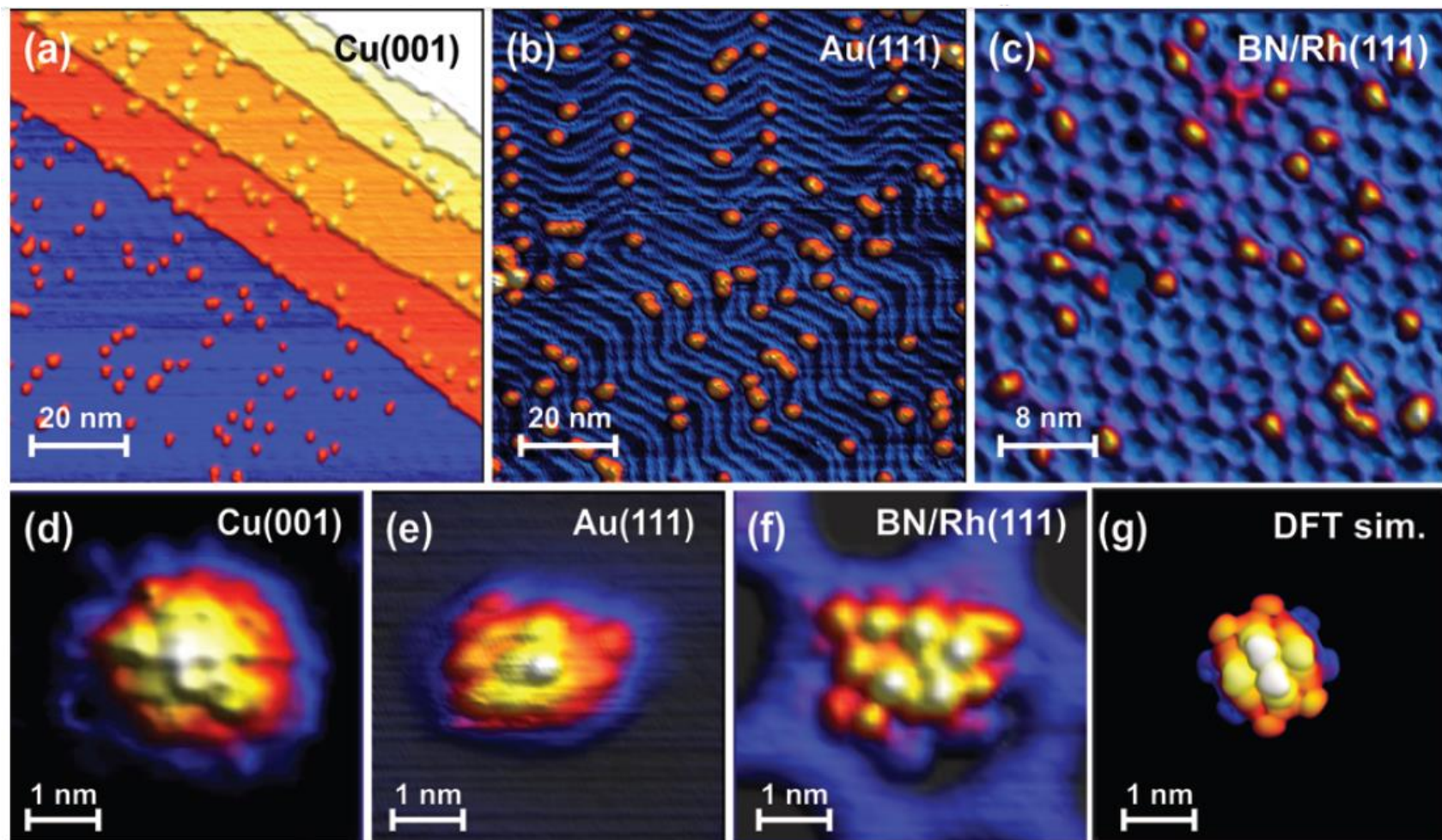


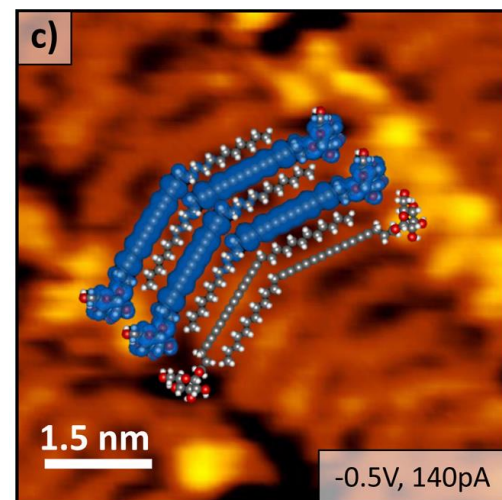
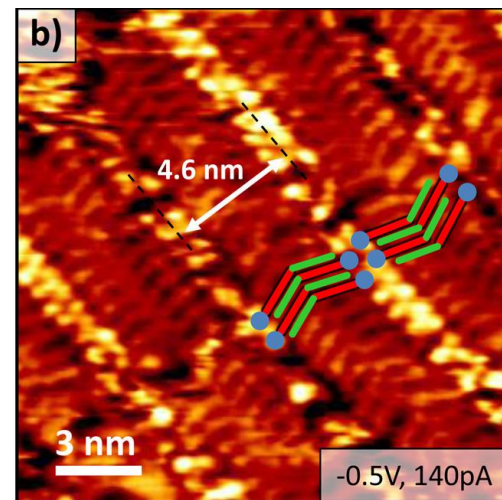
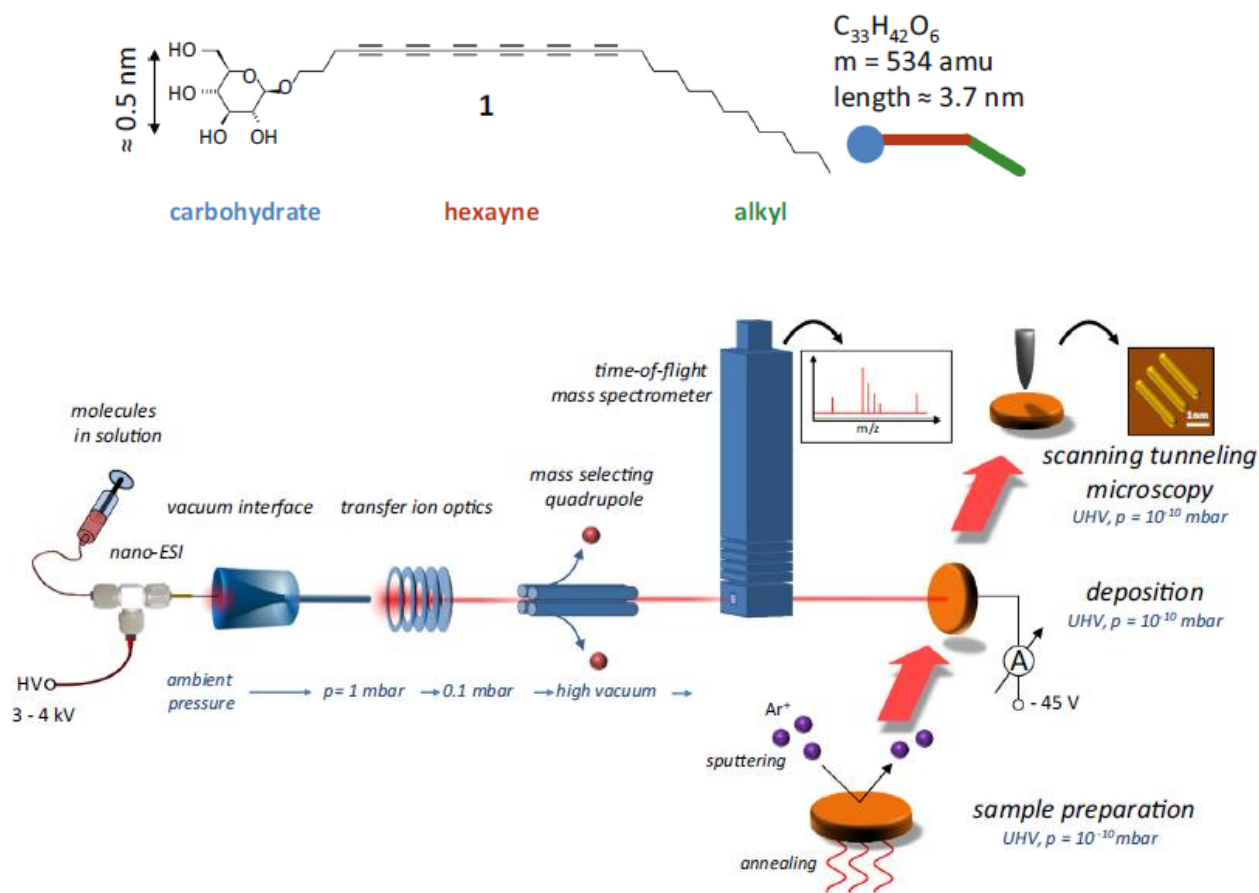
Figure 1. Scheme of the ES-IBD experiment. The protein CytC, displayed in ribbon representation, is ionized by ESI. Ion optics, such as an ion funnel, quadrupoles, and lenses are used to collimate, mass select, and focus the beam. TOF-MS allows access to the chemical composition. Ion beam deposition takes place in ultrahigh vacuum (10^{-10} mbar). The deposition energy can be adjusted, and the ion current is monitored. Samples are investigated in situ by STM (see Supporting Information A for details).

The Quantum Magnetism of Individual Manganese-12-Acetate Molecular Magnets Anchored at Surfaces



Soft-landing electrospray ion beam deposition of sensitive oligoynes on surfaces in vacuum

Gordon Rinke^a, Stephan Rauschenbach^{a,*}, Stephen Schrettl^b, Tobias N. Hoheisel^b, Jonathan Blohm^{a,1}, Rico Gutzler^a, Federico Rosei^c, Holger Frauenrath^b, Klaus Kern^{a,d}

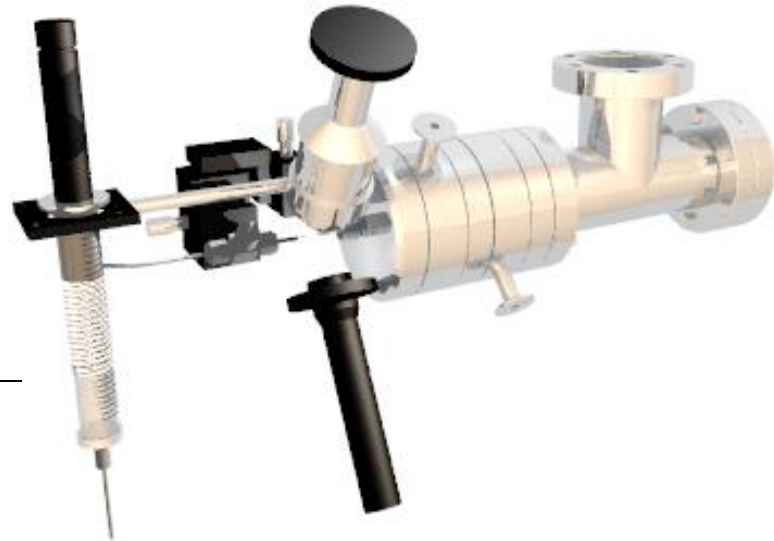


Conclusions



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In-situ UHV electrospray deposition has opened up a range of surface science techniques to large, fragile and non-volatile molecules from single molecule magnets to proteins.



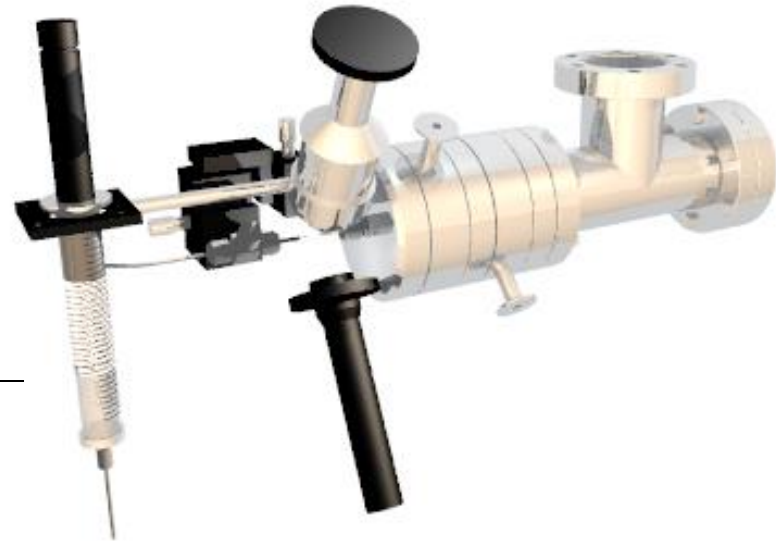
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Thanks



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Nottingham

Neil Champness, Chris Satterley, Louise Mayor, Andrew Britton, Matt Weston, Karsten Handrup, Alex Saywell, Harry Anderson, Luis Perdigao, Simon Svatek, Ben Taylor, Achim Schnadt, Peter Beton, Karina Schulte, Annette Pietzsch, Rob Temperton, Andy Gibson, Victoria Richards



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