



CITY UNIVERSITY
LONDON

Optical Fibre Sensors for Cocaine

Dr Ewan Galbraith (EKG), Dr Hien Nguyen, Cargo Screening Network Meeting, Sheffield.

10th November 2009



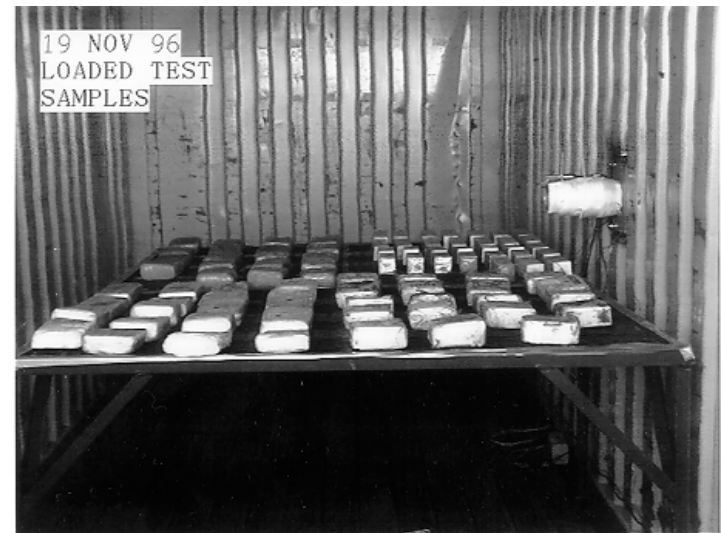


CITY UNIVERSITY
LONDON

Vapour vs. Particulate Sensors

- Cocaine vapour very difficult to detect at RT (IMS can only detect at 50°C or air flow and a crate full of unadulterated cocaine-see picture)
- 0.11 ppb cocaine in air directly over pure open sample at RT (3ngL^{-1} , $P_v = 0.14 \times 10^{-7}$ Torr)
- Sniffer dogs trained to detect methyl benzoate, main common volatile impurity.

Dindal *et al.*, *Analyst*, **2000**, 125, 1393–1396
<http://www.techmondial.co.uk/assets/documents/WCCE-05.pdf>





CITY UNIVERSITY
LONDON

Vapour vs. Particulate Sensors

- Methyl benzoate (P_v 0.41 Torr) used as solvent, in perfumes and fertilizers ie many false positives
- Also a biomarker of mold inside buildings
- No highly selective or specific recognition motif exists
- EDME present in **16 ppm** ($120 \mu\text{gL}^{-1}$) directly over pure sample of EDME, not cocaine.
- EDME trace increased by UV irradiation.

Neudorfl *et al.*, *Anal. Chem.* **1997**, 69, 4283-4285





CITY UNIVERSITY
LONDON

Some Formulae

cocaine

ecgonine methyl ester (EME)
Thermal product of higher P_v

ecgonidine methyl ester (EDME)
UV irradiation product

methyl benzoate
Volatile head-space indicator





CITY UNIVERSITY
LONDON

Proposal

- Home Office (Dr Duncan Harding) asked us to focus on cocaine in solution with ultimate target vapour detection.
- Also highlighted some key points:
 - Critical to minimise false positives
 - Improved sensitivity over existing systems
 - Vapour is a challenge for engineers but very desirable





CITY UNIVERSITY
LONDON

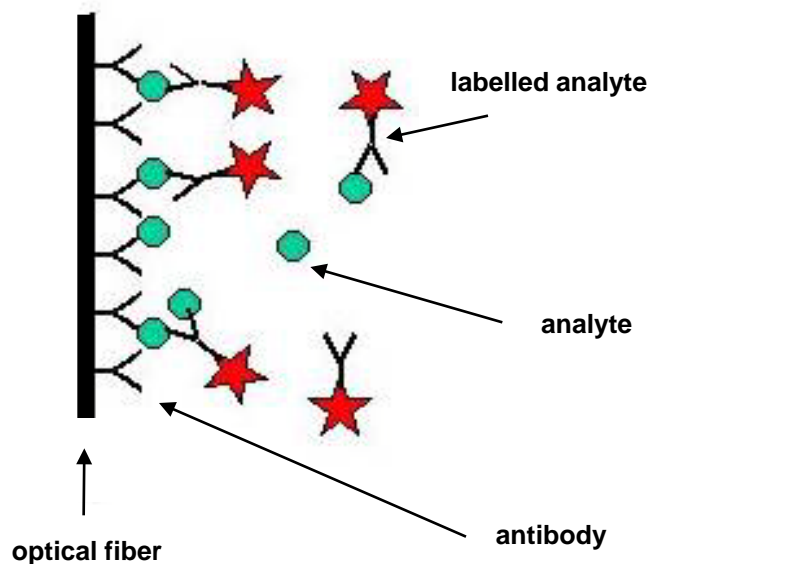
Two alternative approaches

- Biosensor
 - Natural receptors such as antibodies
 - Very high selectivity
 - Very high sensitivity
 - Limited shelf life
 - Relatively expensive
- Chemosensor
 - Synthetic receptors
 - Often more stable and robust
 - Relatively cheap
 - Less selective
 - Very high sensitivity (particularly conjugated polymers).

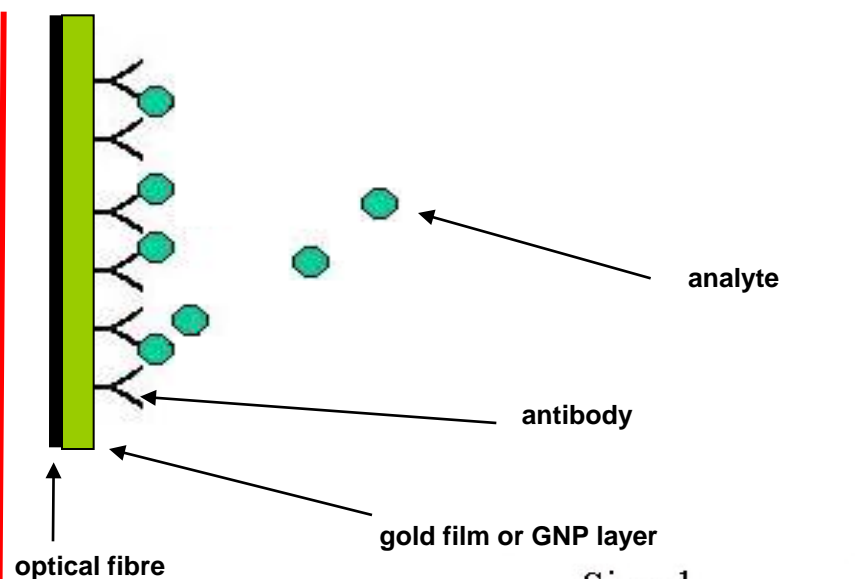
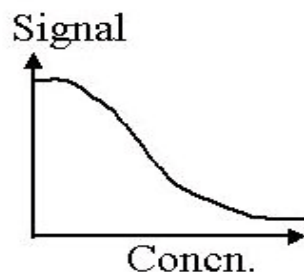




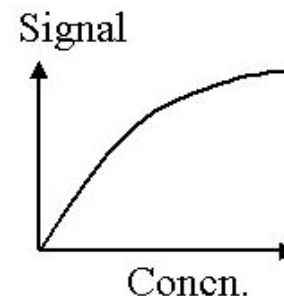
Biosensor Approaches



Competitive binding assay:
analyte and fluorescent
labelled analyte compete
for antibody binding sites



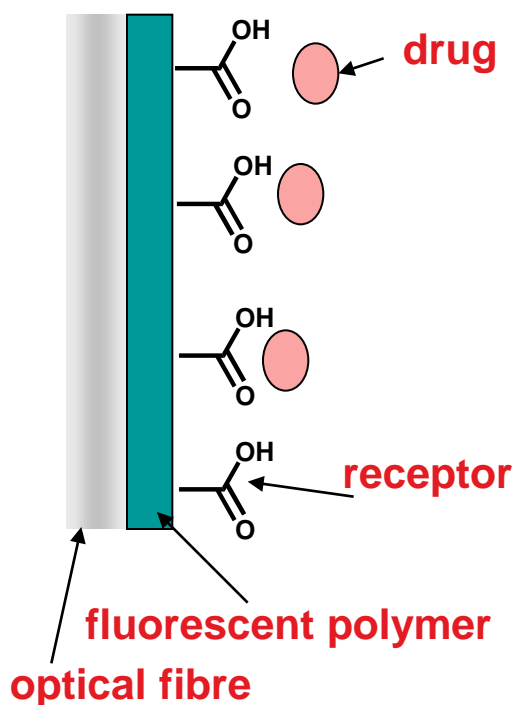
**Non-competitive binding
assay:** analyte binds
directly to antibody binding
sites.



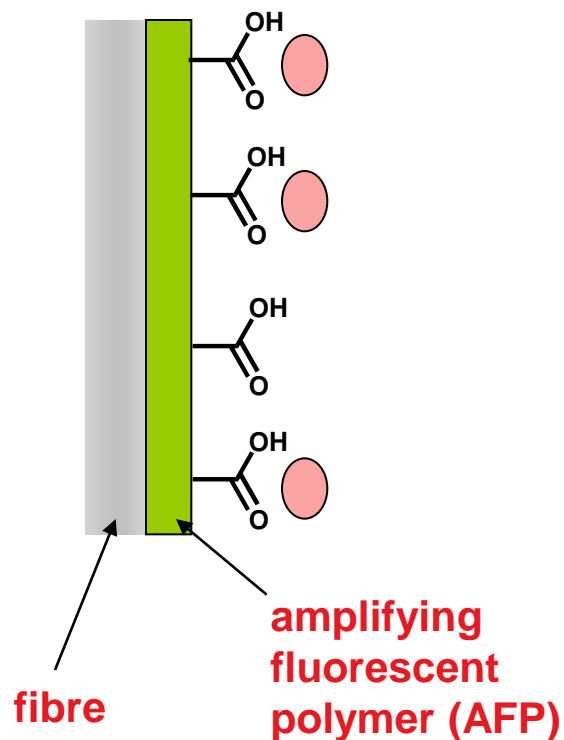


Chemosensor Methods

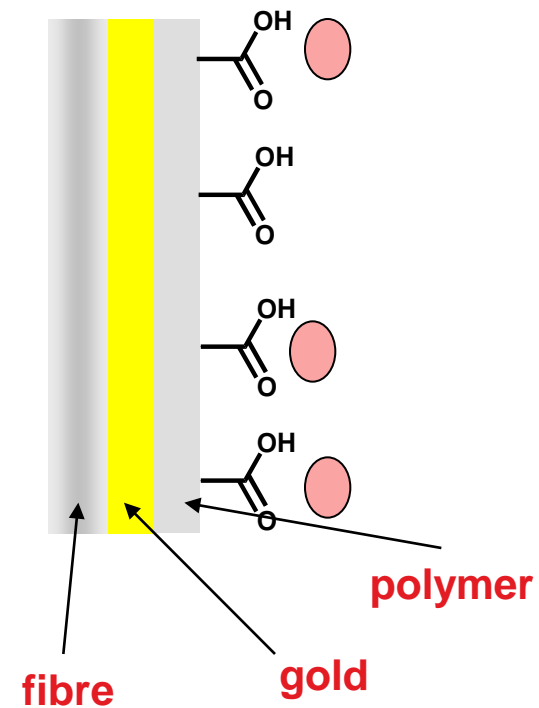
Single molecule fluorescence



Amplifying fluorescence



SPR





CITY UNIVERSITY
LONDON

Brief

- EKG to design and synthesize optical fibre based sensor for cocaine in solution
- Seek a design which will enable a fluorescence enhancement response to cocaine
- Ideally find a wavelength shift response model
- After proof of concept undergo 2 processes
 1. Ensure/achieve high sensitivity
 2. Look to engineers for preconcentration method.



CITY UNIVERSITY
LONDON

EKG Plan

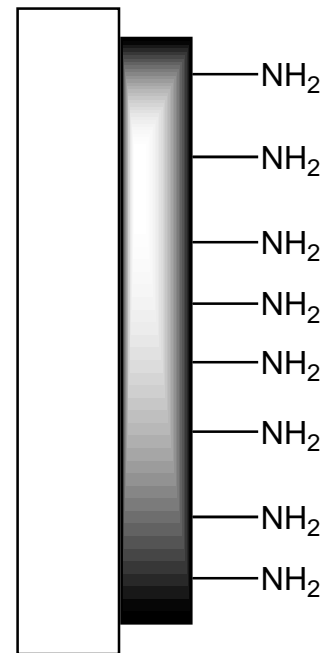
- Based on aptamer-cocaine binding and subsequent folding
- Highly specific and reversible

- Several ways to utilise this specific response.
 - polymers (both conjugated and non-conjugated), gold thin film, gold nanoparticles, classic fluorescence donor/quenchers, streptavidin-biotin conjugates, chemisorption.



EKG Plan

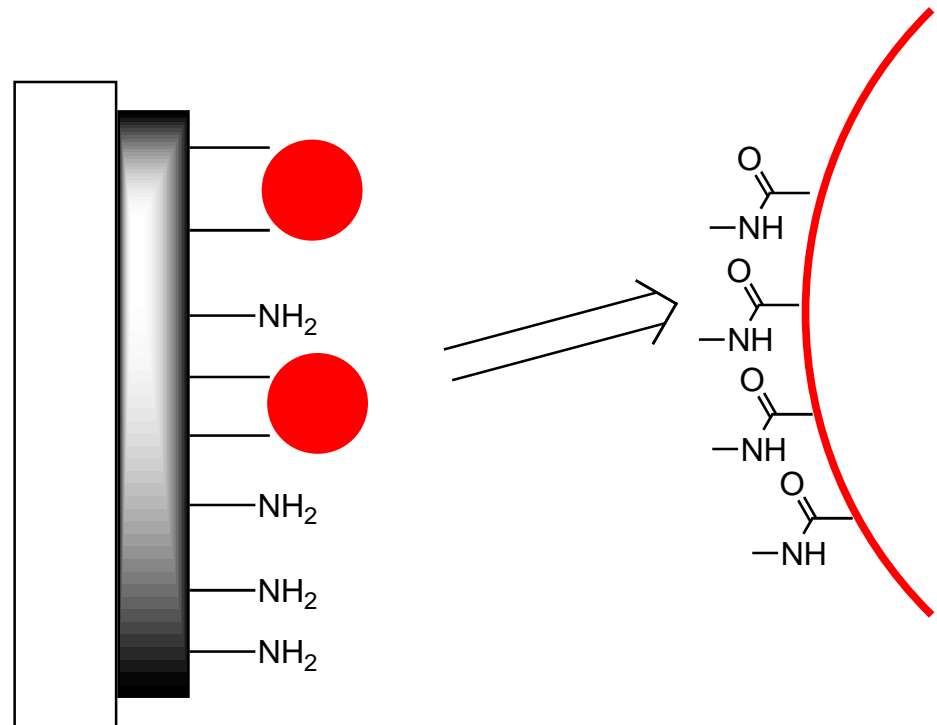
- Fibre preparation
 - Clean exposed core with acid treatment
 - Silanization process performed as per literature precedent
 - Ready to be coupled via EDAC to carboxy functionalised nanoparticles/biomolecules.





EKG Plan

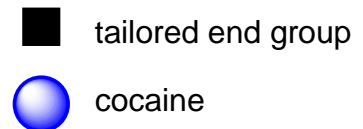
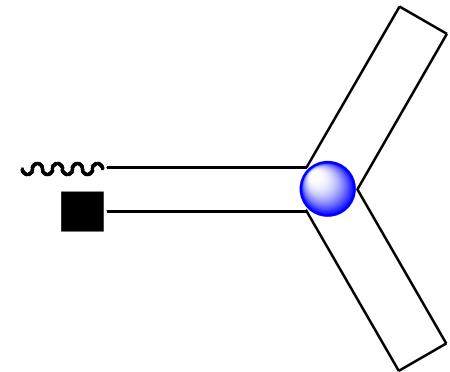
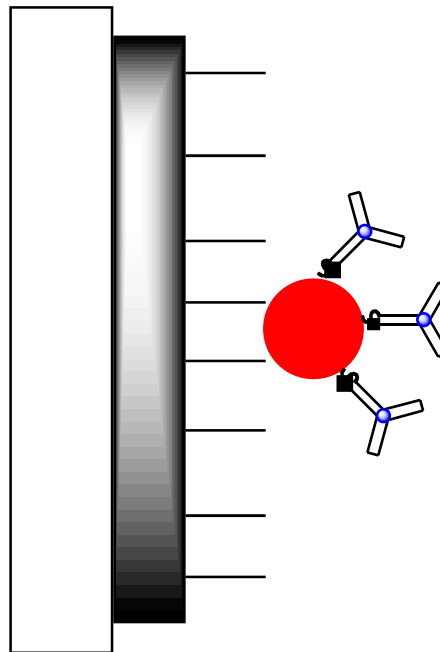
- Qdot immobilisation.
- In vitro supply Qdots with max emissions from 500-800 nm. Current plan is Qdot 655 due to favourable absorption profile.
- Free amines capped after Qdots immobilisation to prevent non-specific interactions.





EKG Plan

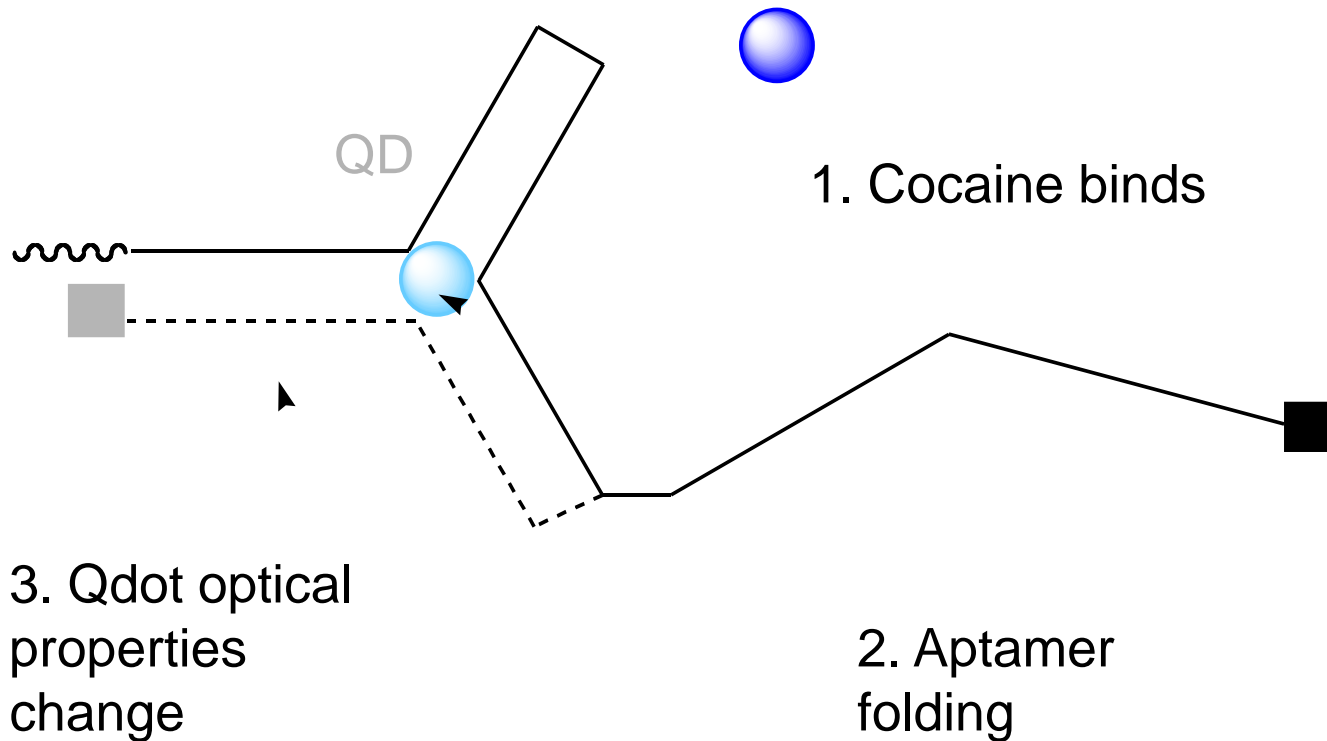
- Cocaine templated QDot functionalization
- Prevents steric crowding at surface ie limiting sites so folding can occur.
- Simply wash excess cocaine with PBS



- Aptamer sequence: AGACAAGGAAAATCCTTCAATGAAGTGGGTCG



EKG Plan



Possible emission wavelength shift, influence of end group?

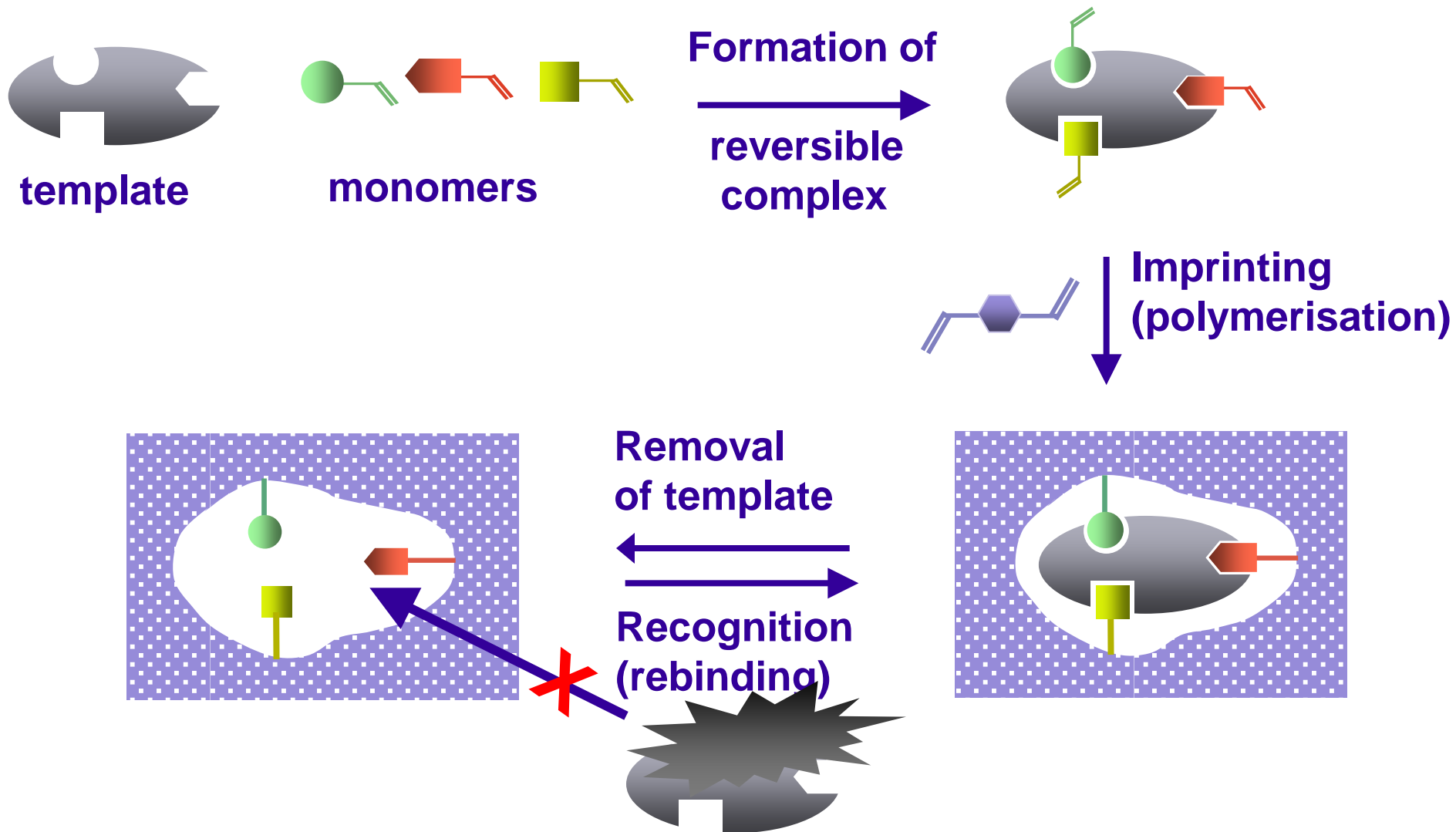


EKG Plan

- Aptamer ensures less false positives as specific to cocaine
- Quantum Dot should ensure high fluorescence intensity, sensitivity and narrow emission response
- Potential to be tunable by end group
- Novel modification of Qdots provides less of overlap with other published non-optical fibre systems
- Optical Fibre (surface) Immobilised
 - More sensitive
 - Easier to purify/prepare (desalting, centrifugation)
 - Re-usable once constructed with expected finite shelf-life (1 month predicted based on precedent)
 - Portable, low weight device envisagable.

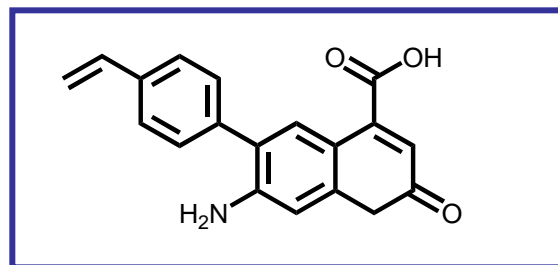
What is molecular imprinting?

.....making artificial "locks" for "molecular keys"

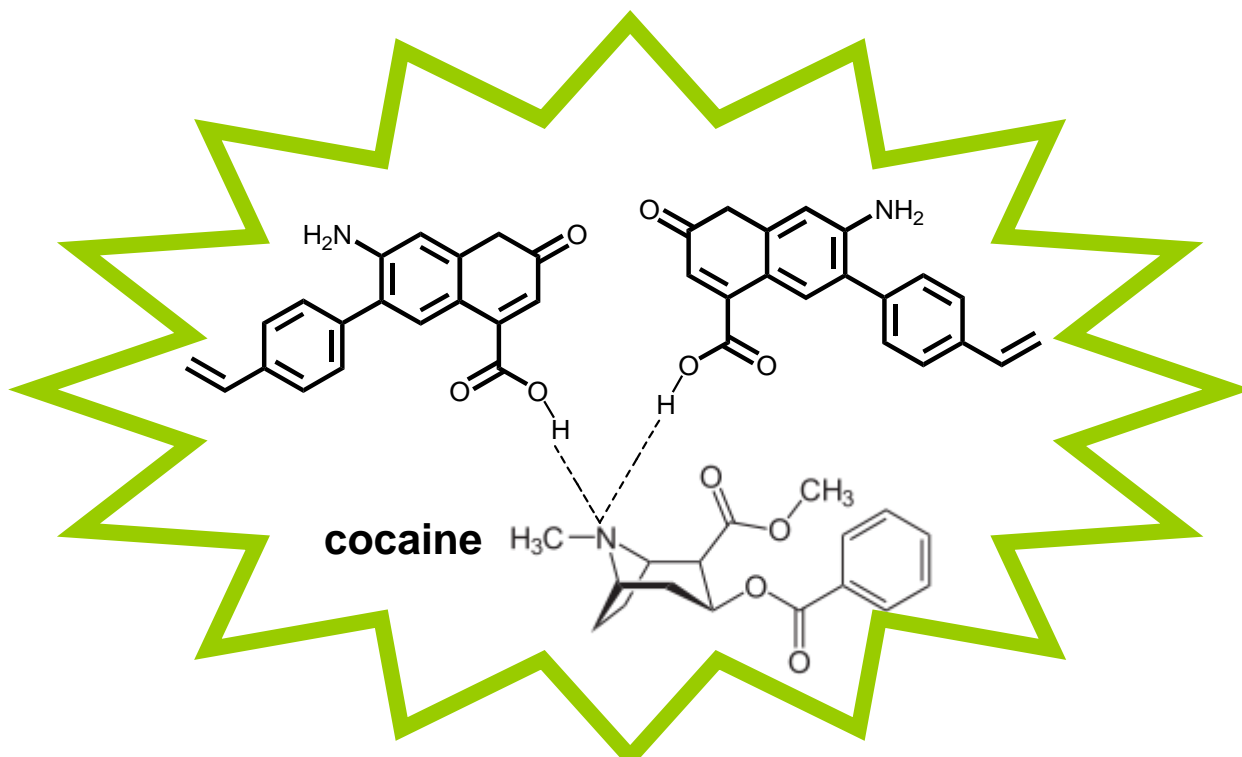


Fluorescent MIP sensor for cocaine

Fluorescent functional monomer:

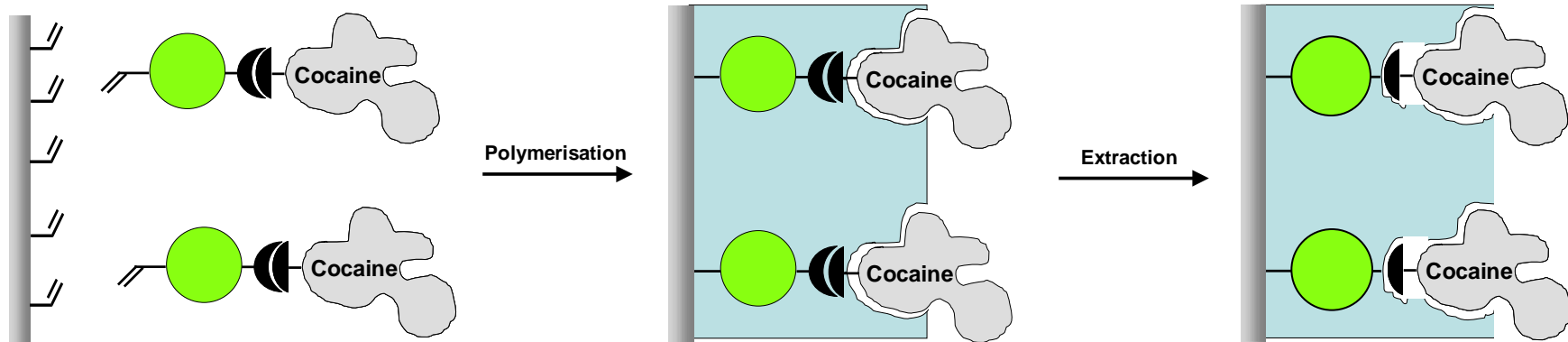
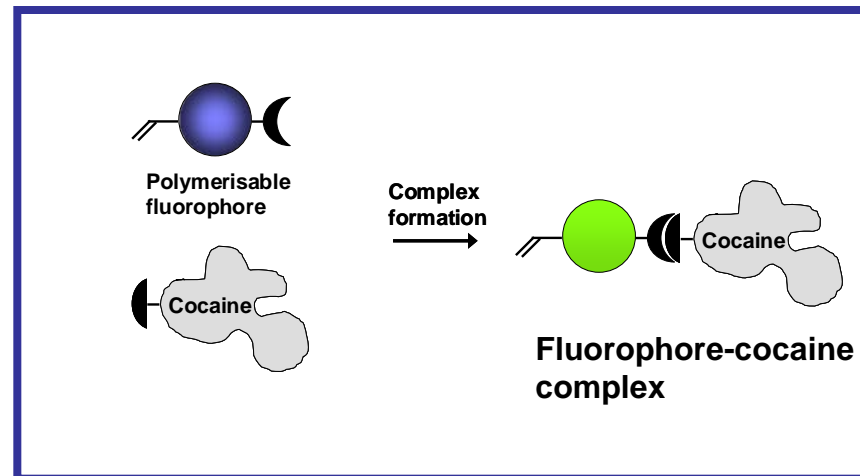
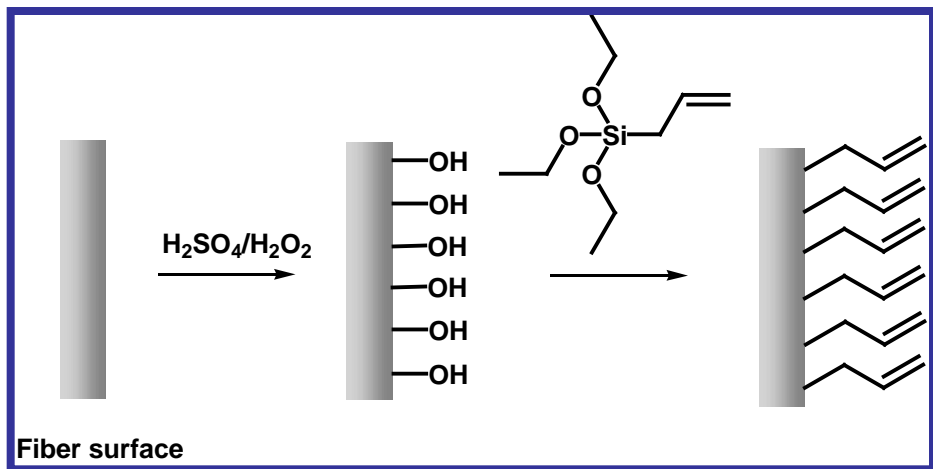


- 1) Rigid structure, minimising the rotation around binding sites
- 2) exhibit fluorescence changes upon binding to the template



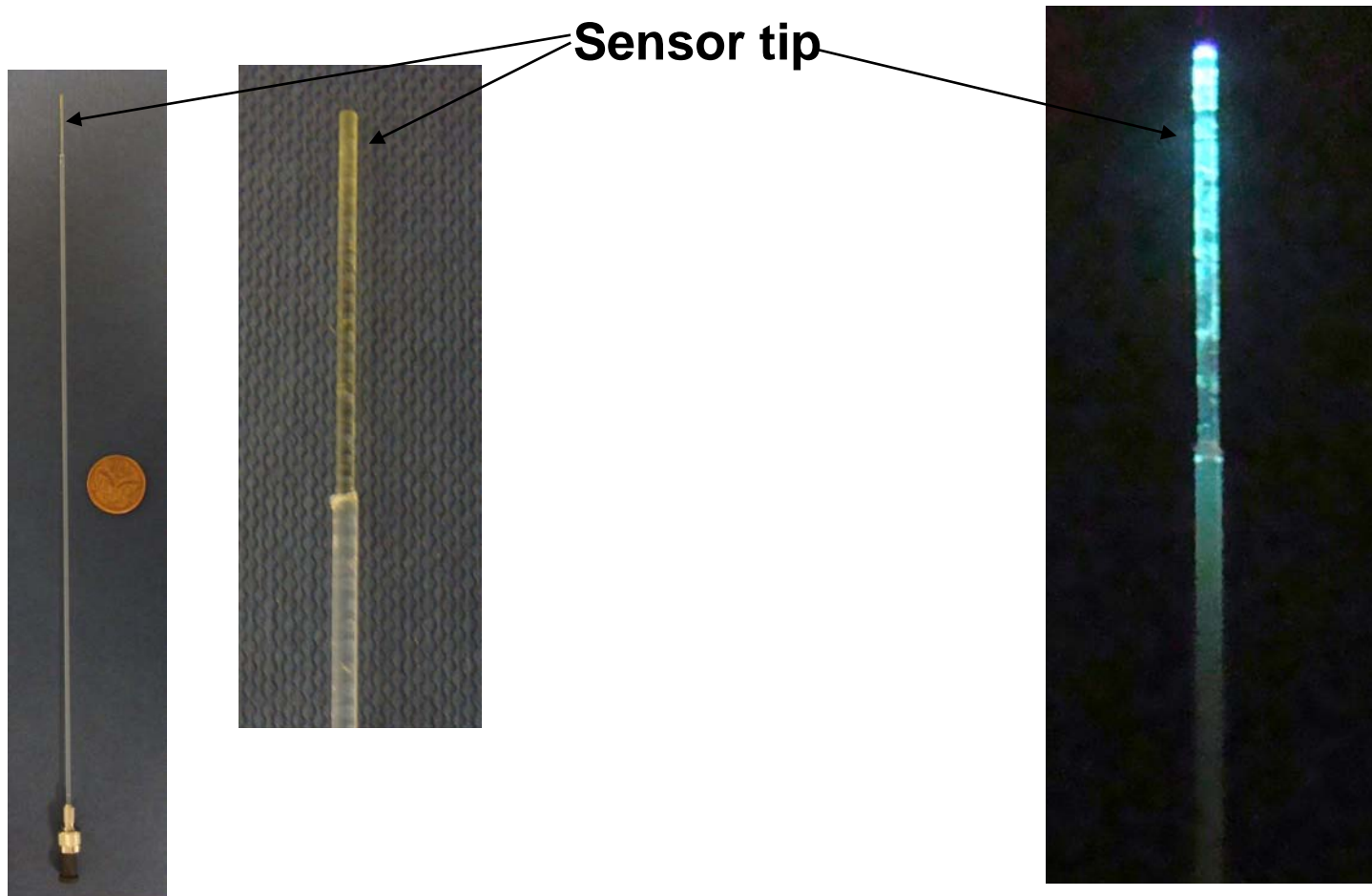
Fluorescence switch-on in
the presence of cocaine

MIP film on fibre surface



Rebinding: Fluorescence switch-on

Cocaine sensor probe

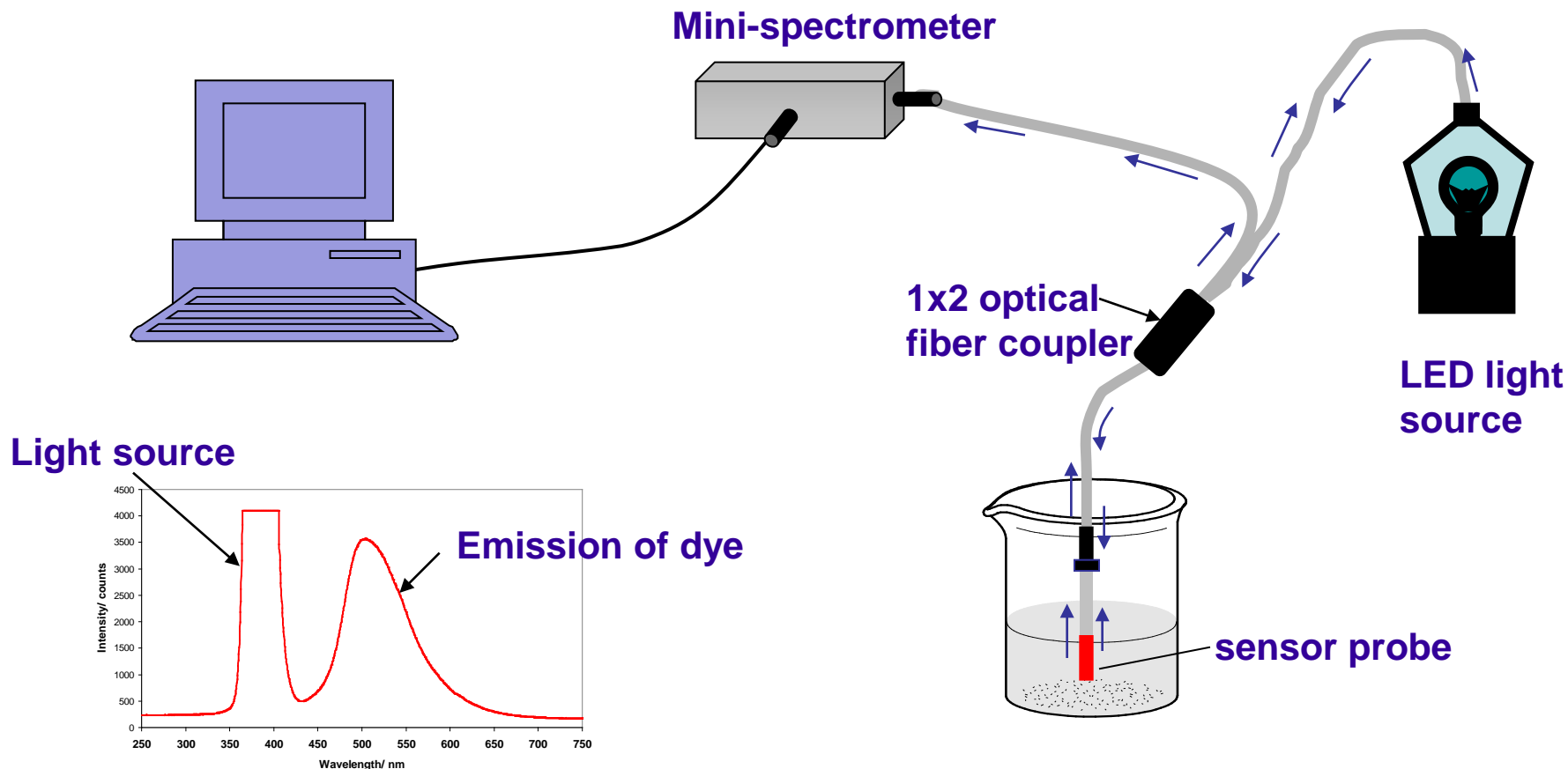


Sensor tip

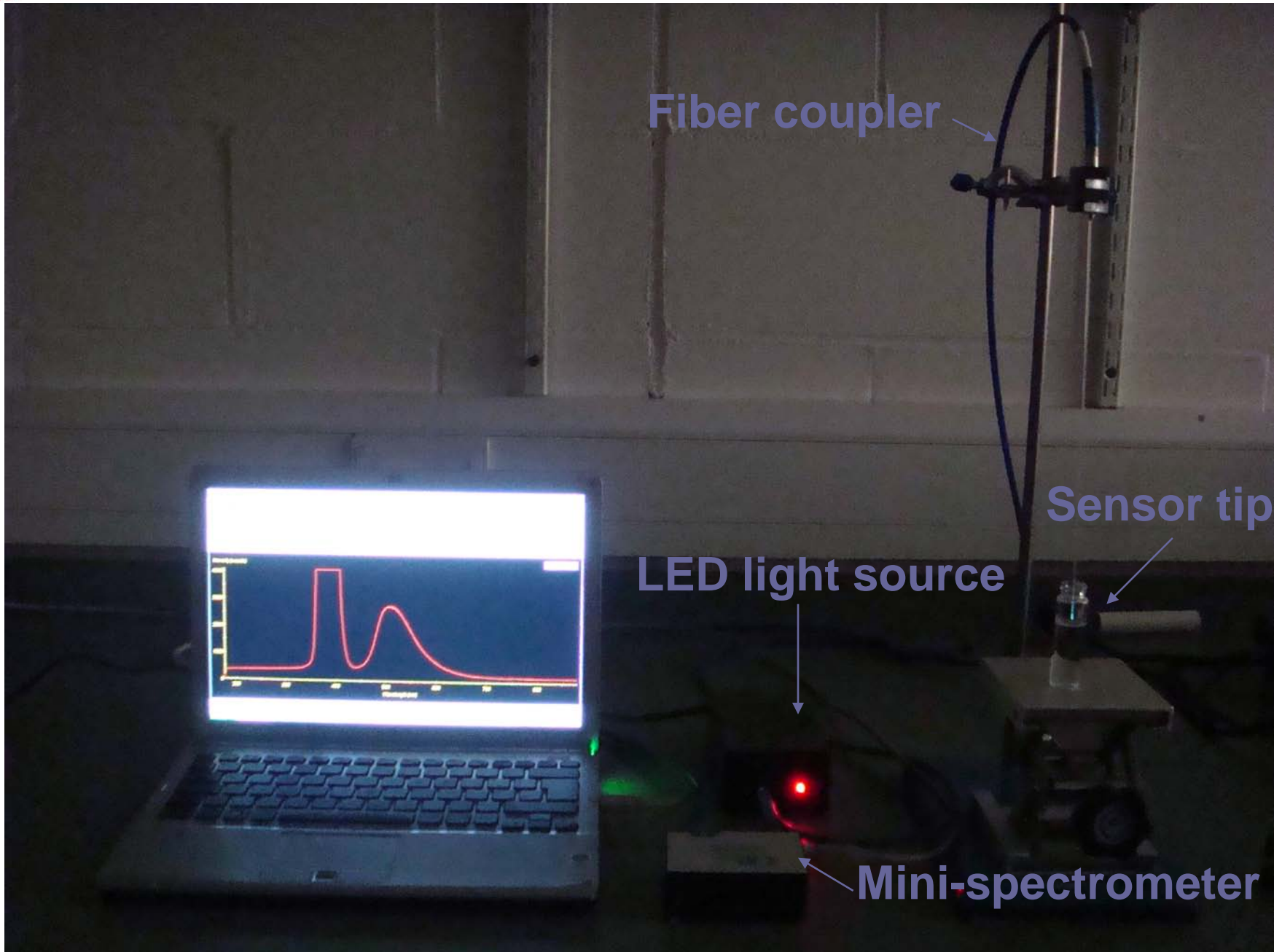
normal conditions

UV 375 nm

Experimental set-up

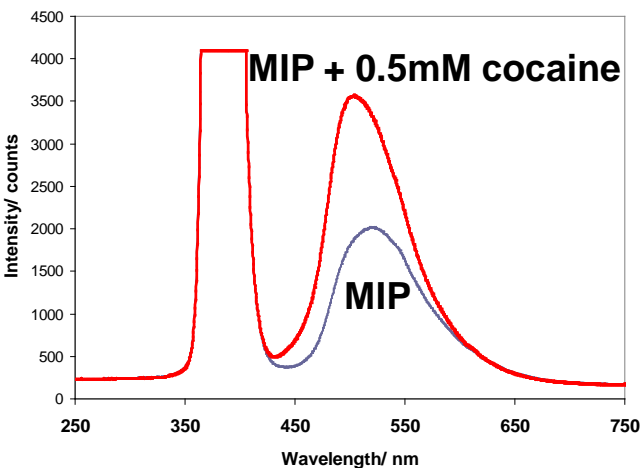


- An LED light source is used to excite the material.
- A 1x2 fibre coupler is used to launch the excitation light to the sensing material and to direct the emitted light to the spectrometer.
- The detection is done using a mini-spectrometer

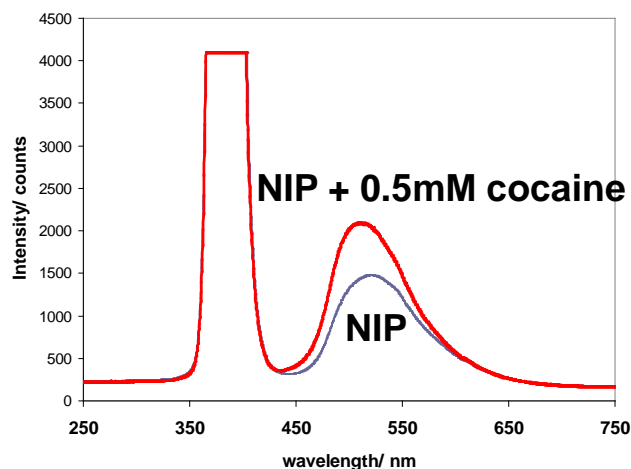


Preliminary results

MIP sensor

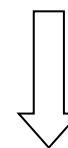
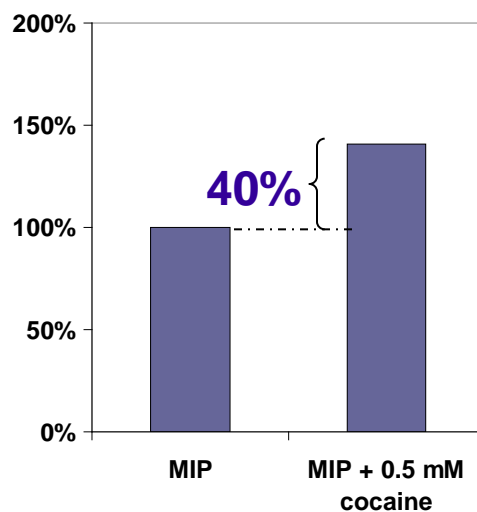
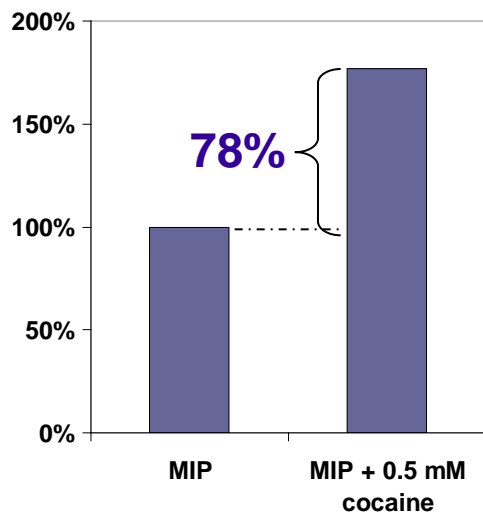


NIP sensor - control



➤ Both MIP sensor and NIP sensor exhibit fluorescence enhancing with adding cocaine.

➤ MIP sensor responds to cocaine more than NIP sensor and shows a shift to shorter wavelengths.



Imprinting effect, and selective recognition sites exist in the MIPs