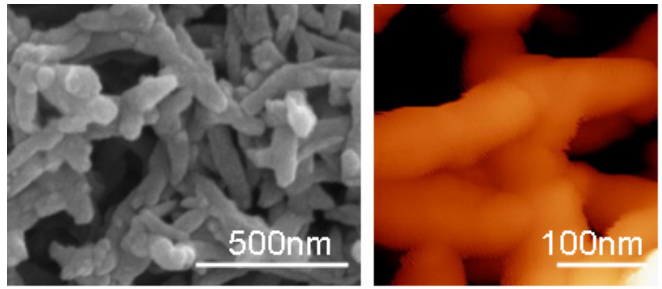
Towards the development of adaptive nanostructured platforms



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Chemistry Solutions
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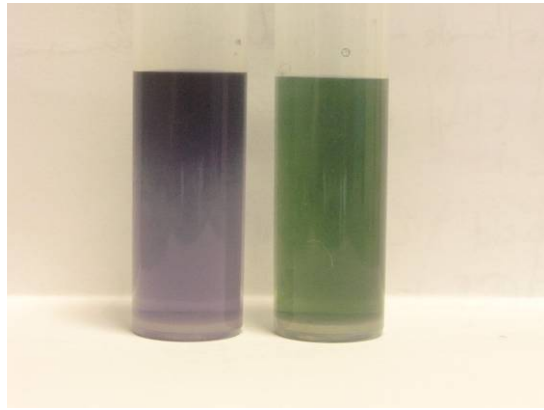
Outline

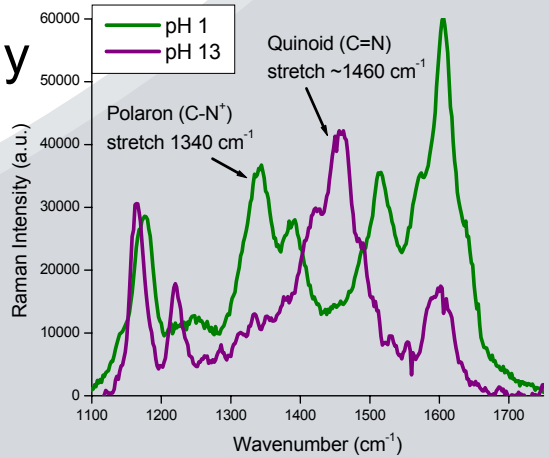
- Adaptive materials
- Conducting polymer nanofibres
- Chemical modification of nanofibres
- Characterisation of functionalised fibres
- Conclusions
- Acknowledgements

Conducting Polymers

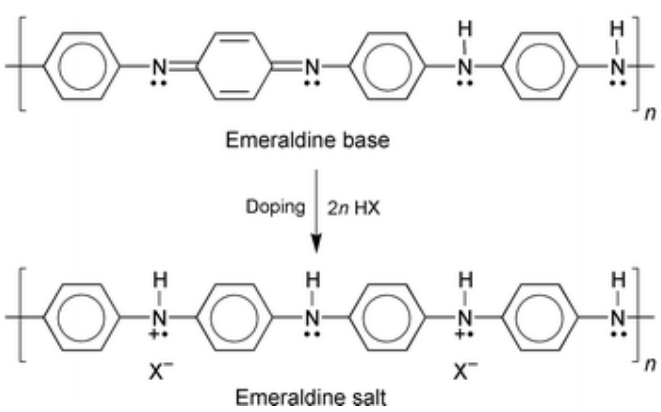
Stimuli responsive materials capable of reacting in an intelligent way to changes in environmental conditions – thus act as ***sensors***.

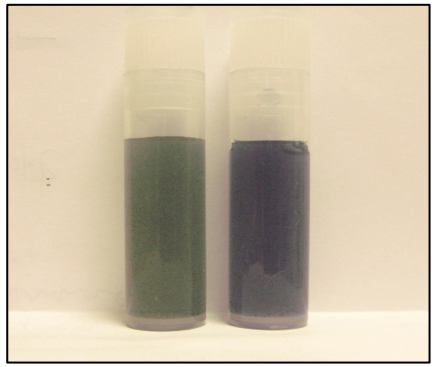


- ✓Change **colour** in response to immediate environment.
- ✓**Spectrocopic fingerprint** changes.
- ✓**Conductivity** can be switched reversibly (10^{-10} S/m → 10^{0} S/m).
- ✓Chemical **structure** changes.
- ✓ **Volume** changes.

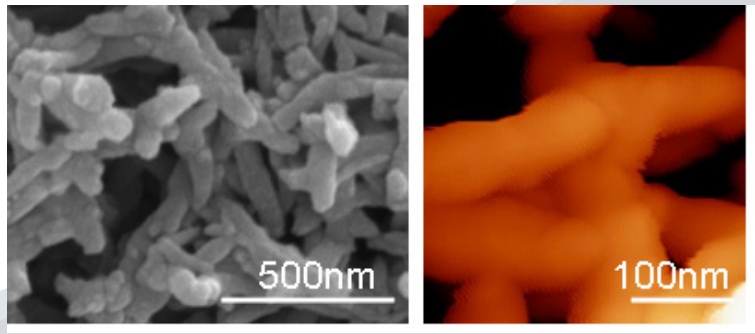


Polyaniline nanofibres



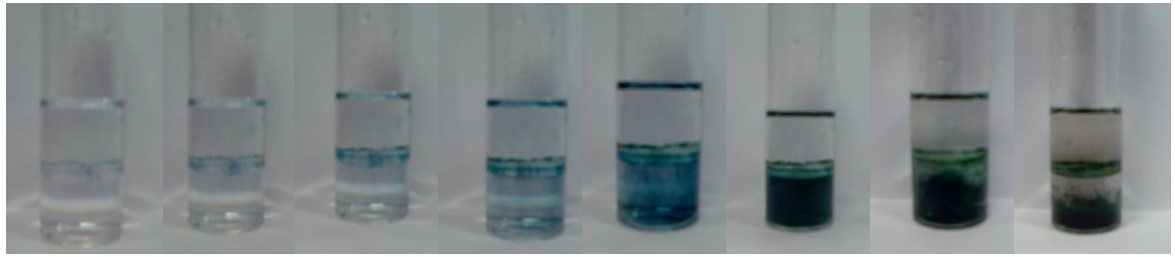


Basing them on ***nanostructures*** means they have increased surface-to-volume ratios.



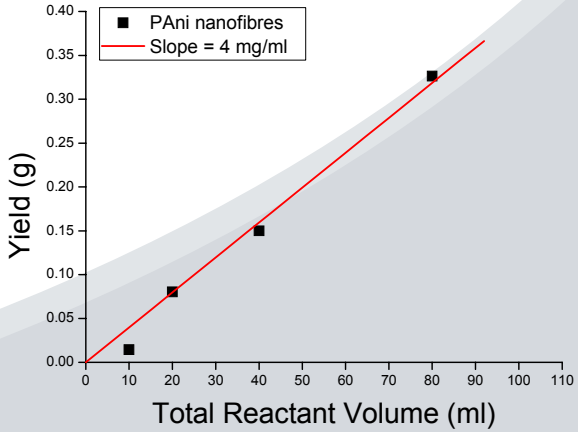
Nanofibre Synthesis

- Inexpensive and convenient to produce.

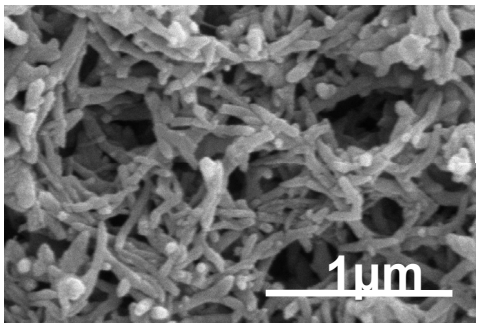


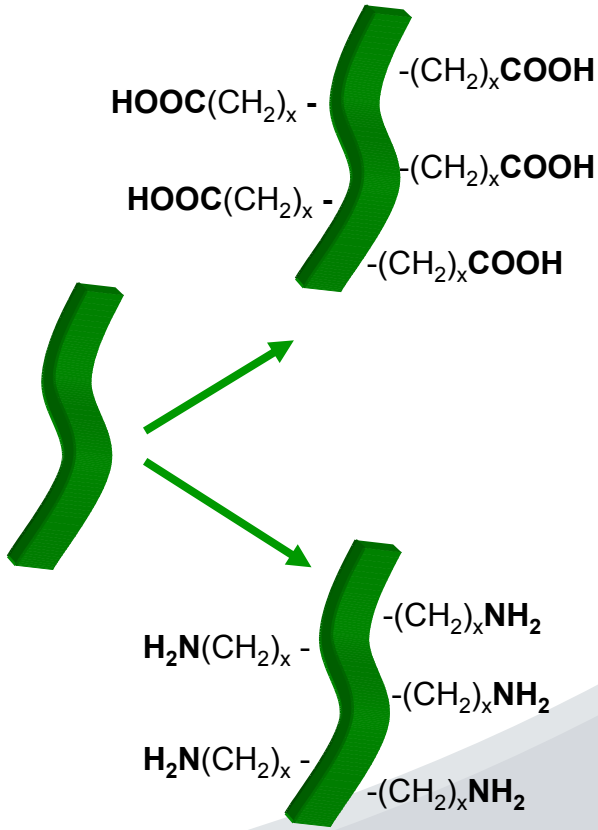
Time (min) = 12 20 30 40 50 60 250 1440 (24hrs)

- Polymerisation complete within 24hrs.
- Yield can be easily **scaled up** by ↑ volume of reactants.
- Convenient purification.

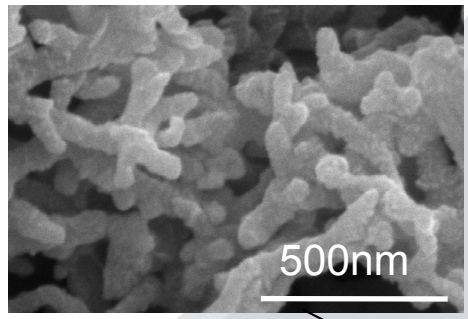


Chemical modification of nanofibres

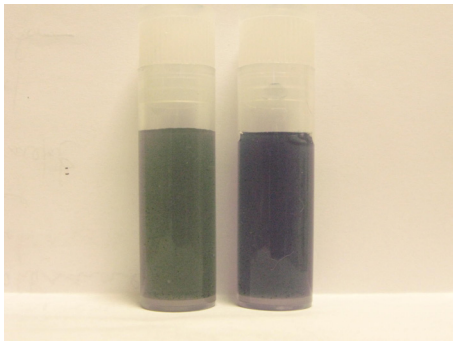


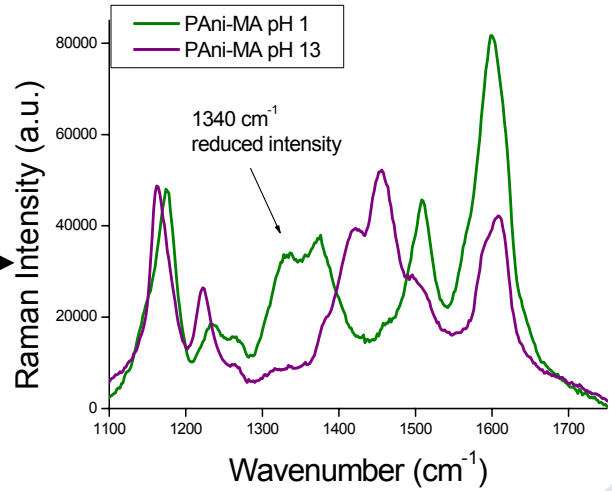


Nanomorphology is maintained!

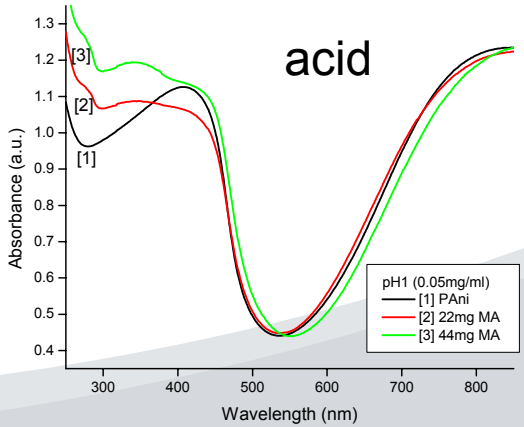


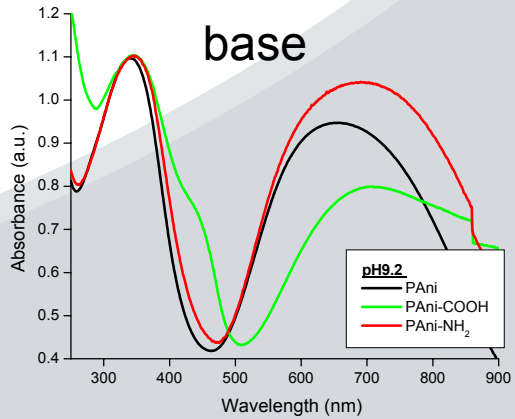
Surface-modified nanofibres switch





Functionalised nanomaterial is responsive to its environment





Evidence for covalent attachment

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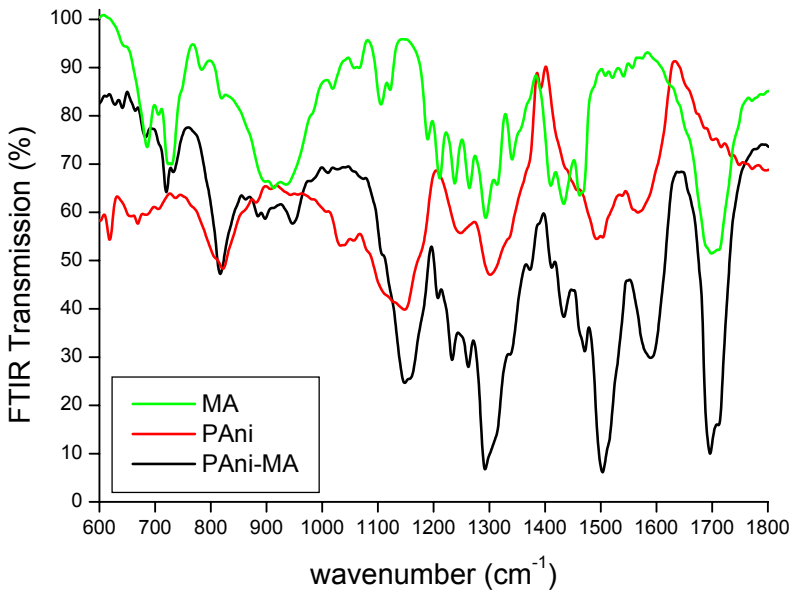
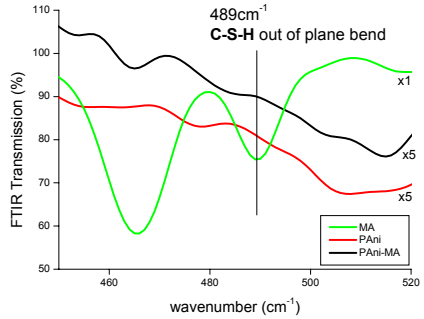
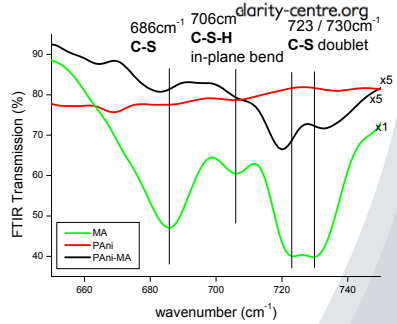
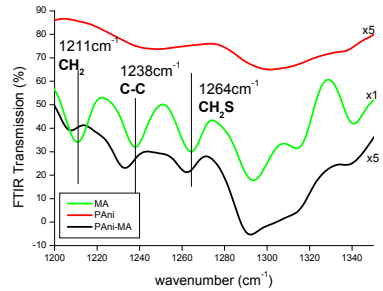
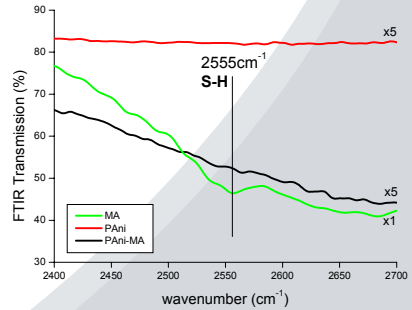
FTIR





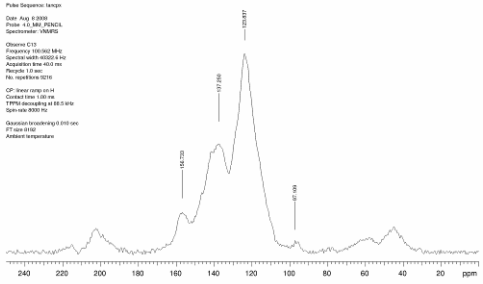




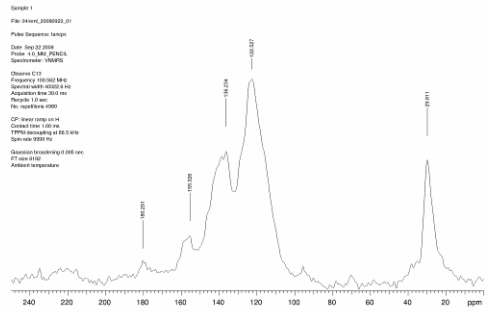


NMR

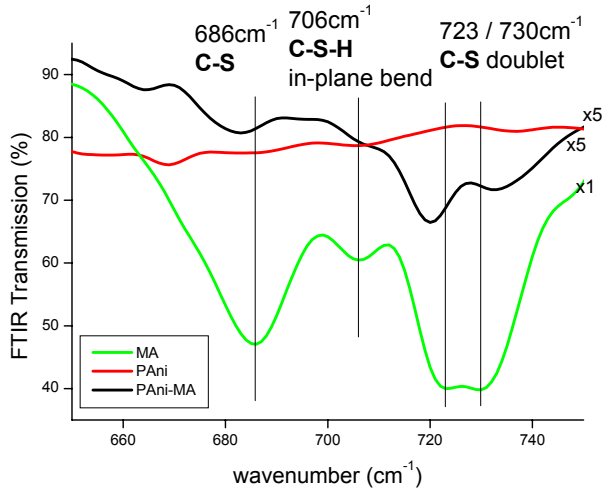
PAni

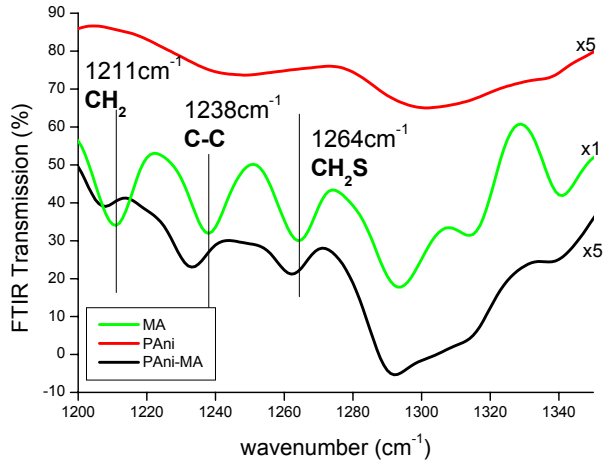


PAni-COOH

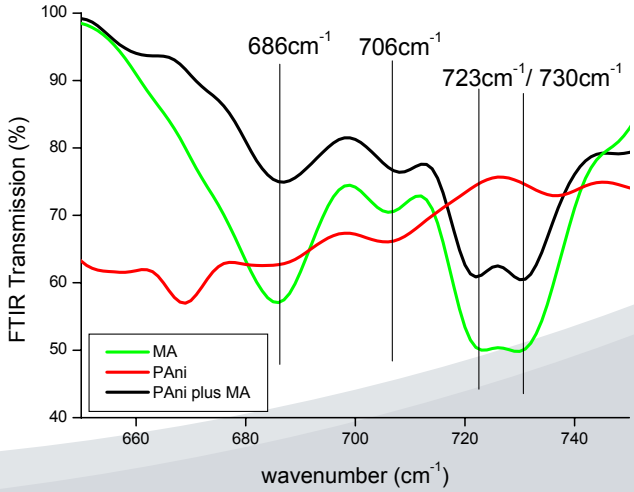


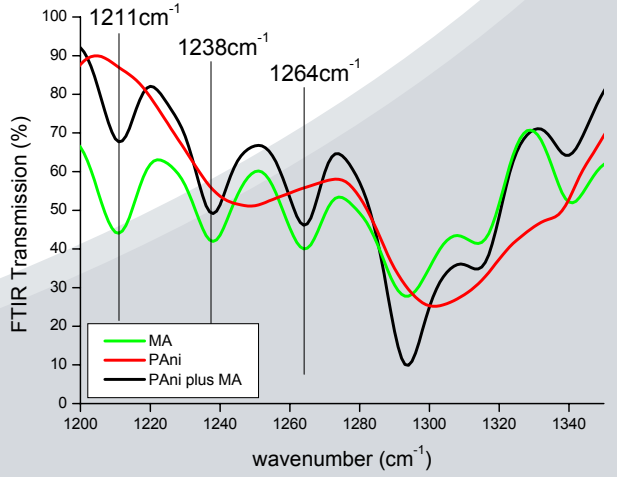
PAni-COOH





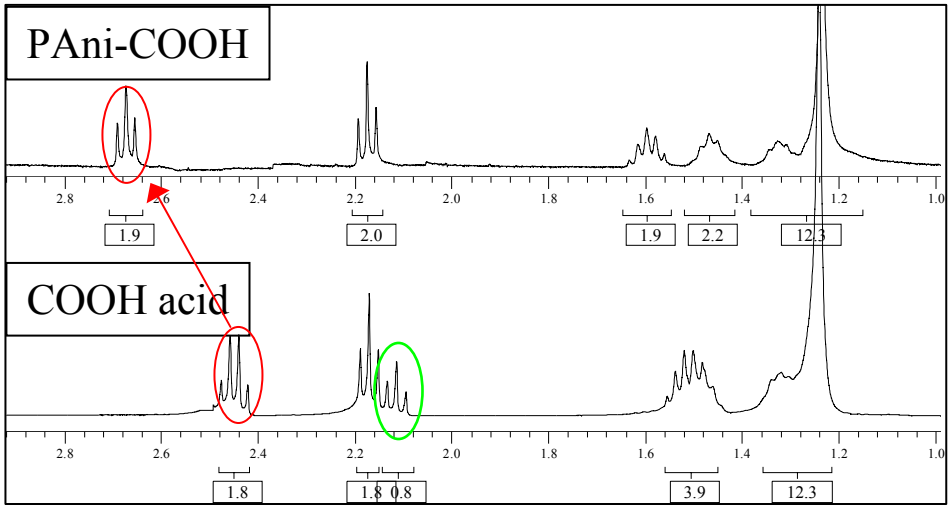
PAni + COOH (no covalent bonding)





NMR evidence

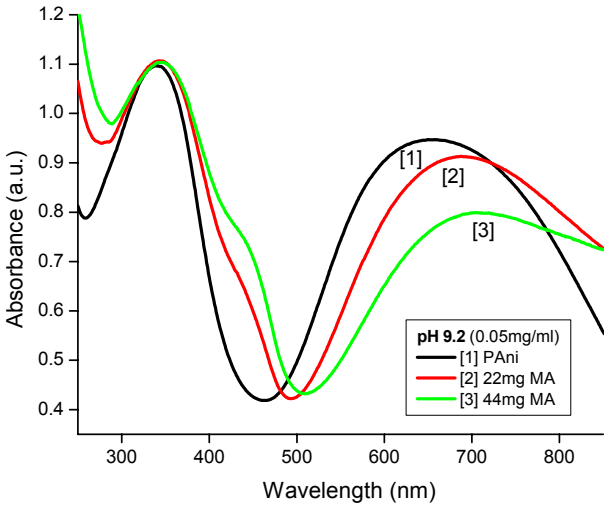
- strongly supports covalent attachment of the MA chain to an electron-withdrawing group.

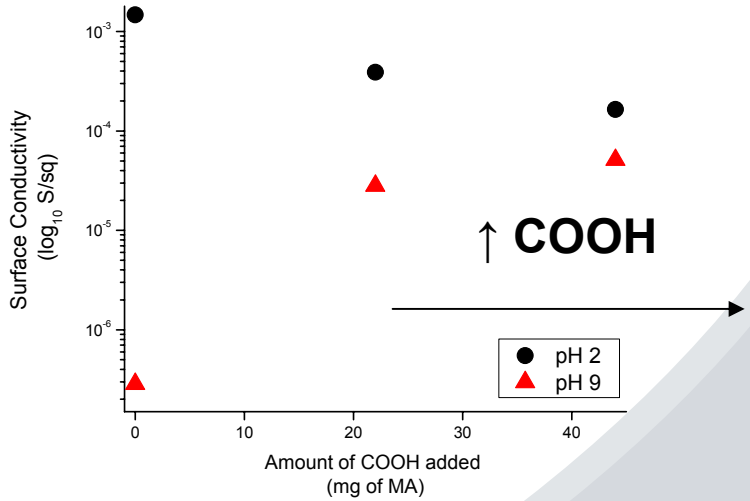


22 protons:
$HS(CH_2)_{10}COOH$

- Triplet @ 2.11 p.p.m. assigned to thiol proton - disappears for PAni-MA.
- General downfield shift for protons in PAni-MA suggests deshielding - consistent with covalent attachment to electron withdrawing units (quinoid ring).
- The shift is accompanied by a change from multiplet to triplet, consistent with the loss of the S-H bond in the PAni-MA.

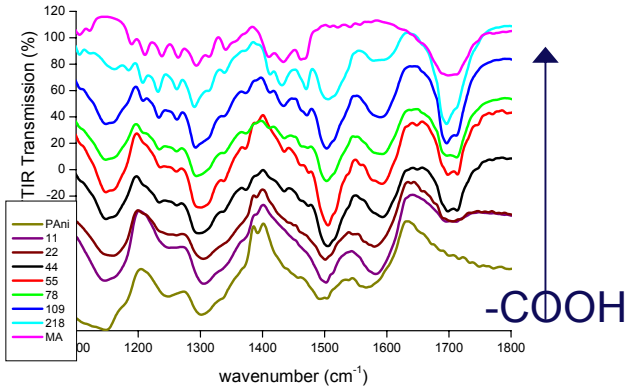
Self-Doping behaviour

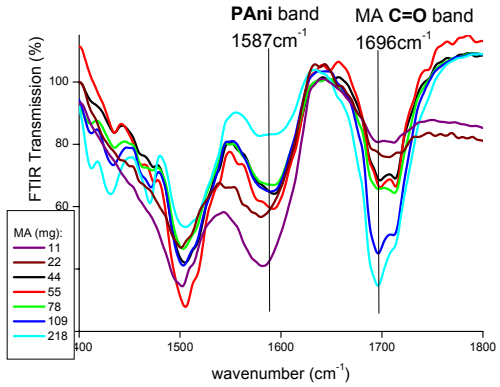


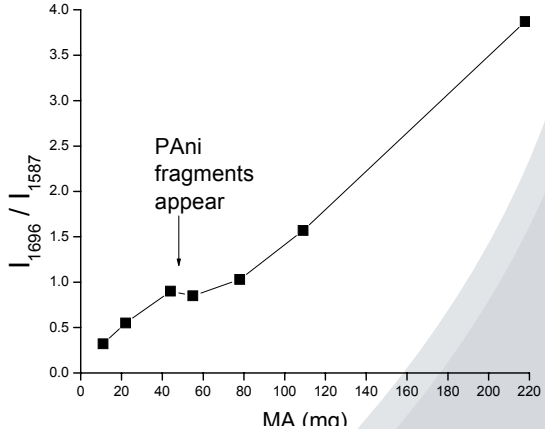


- **Protonation** can occur due to the presence of covalently bound acid side-groups.
- Self-doped nanofibres show enhanced **conductivity** in an alkaline environment.

Controlling the extent of functionalisation



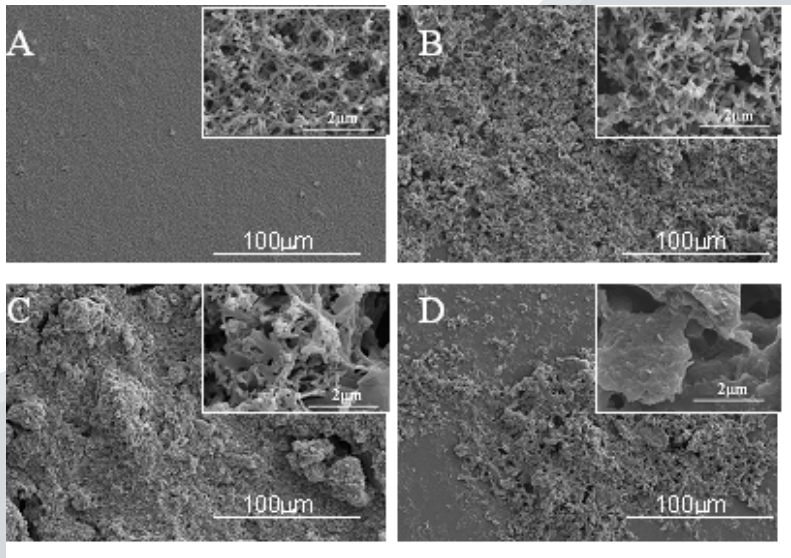




The intensity of -COOH bands scales linearly with the amount of thiol added.

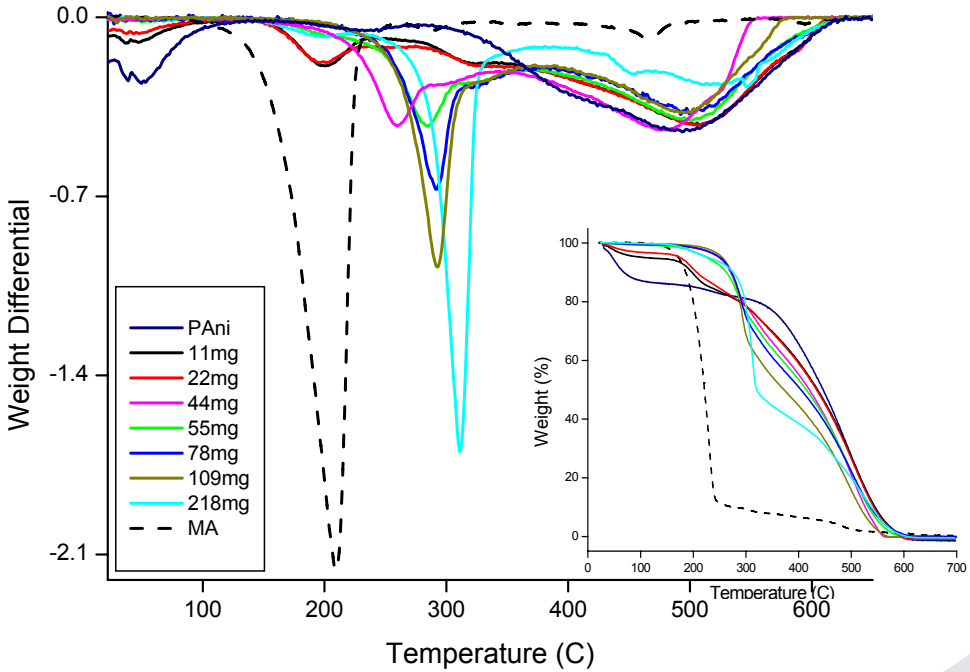
The degree of side-chain attachment can be controllably altered.

PAni nanomorphology is affected by excess functionalisation.



Shown: 0, 44, 109, 218 mg COOH, added to 45mg PAni.

Quantifying the extent of functionalisation

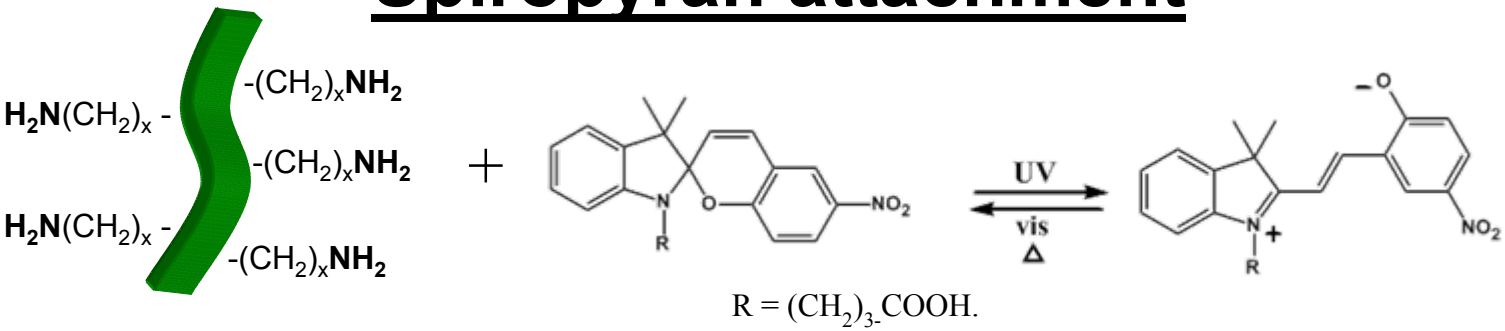


- PAni-COOH fibres show two significant decompositions.
- First peak: a modified PAni-COOH surface component.
- Second peak: unmodified PAni.

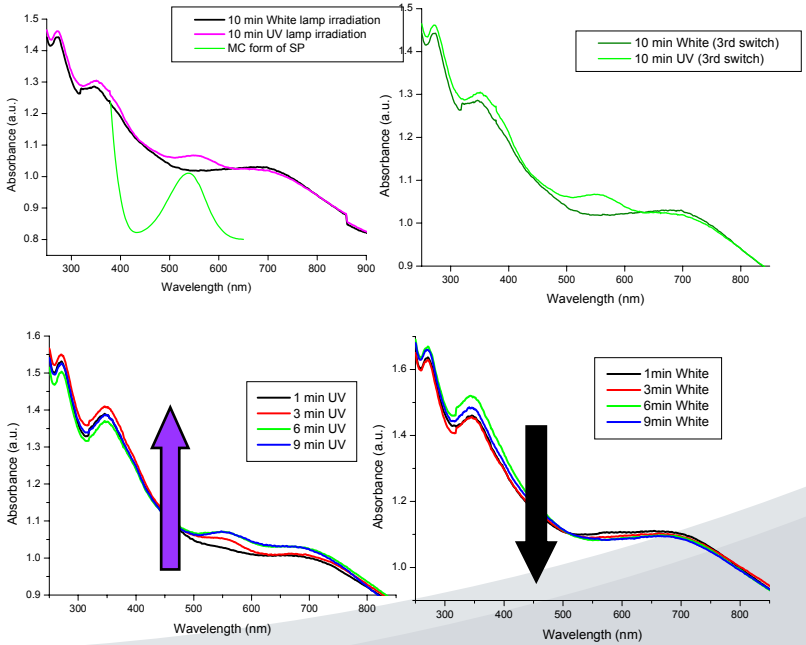
TGA confirms a linear trend in the level of functionalisation

Platforms for further modification

Spiropyran attachment



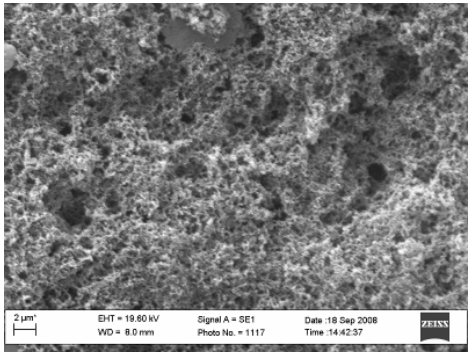
R = $(CH_2)_3$-COOH.

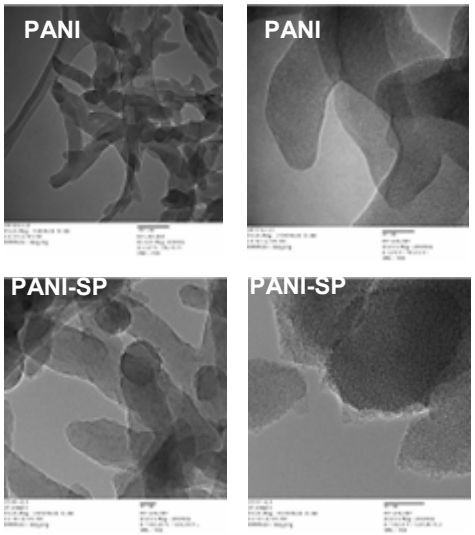


- SP switches to MC form - characteristic peak at 550cm^{-1}.
- This switching can be repeated for three cycles with no observable degradation.

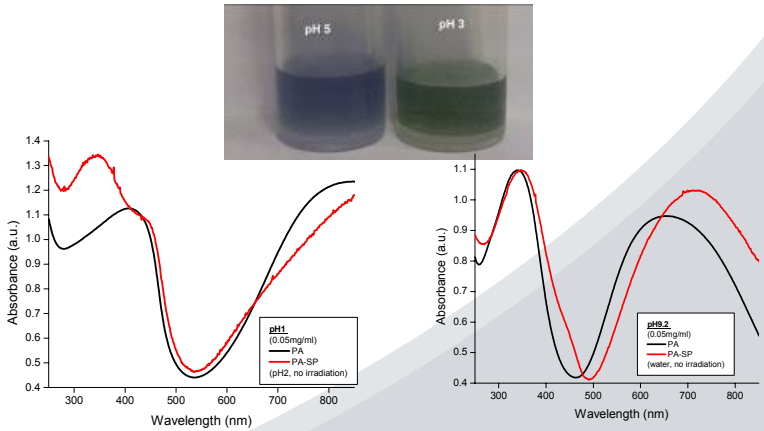
- FTIR support covalent attachment of the carboxylic acid group of SP to the amine group attached to PAni.
- UV (in ethanol) shows SP switching. Swtiching is immediately reversible using white light.

Nanofibres can still be switched



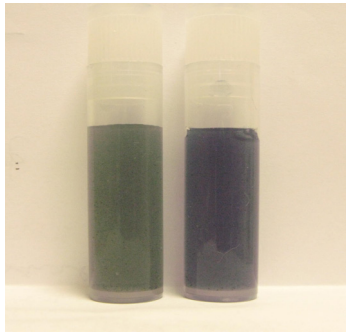


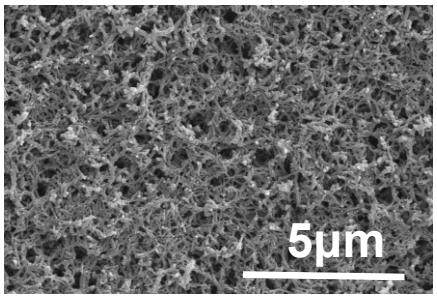
PAni nanofibres can be surface functionalised with spiropyran to produce a nanomaterial with a photoswitchable surface.



Functionalised nanofibres retain the **ability to switch optical properties** in response to changes in the pH of the local environment.

Range of applications for responsive nano-platforms….

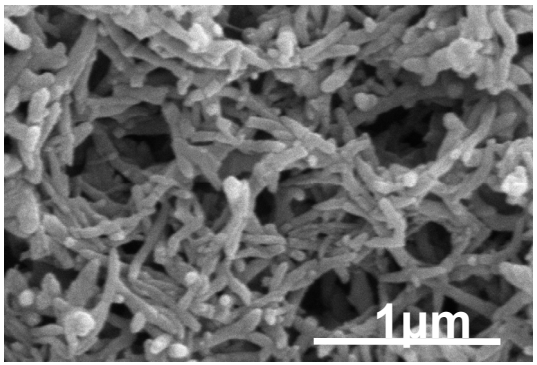


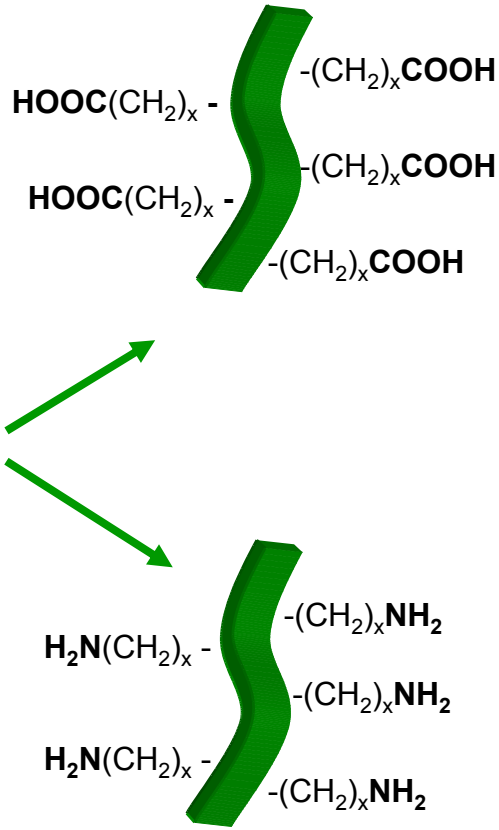


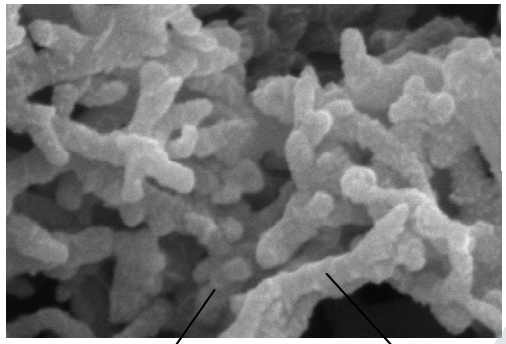
Chemo/ bio sensing
- Anti-body/ virus detection
- Glucose oxidase detection
- Medical and industrial gas monitoring

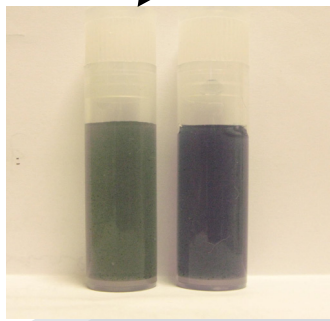
Energy storage devices
Transducers (eg, for immunoassays)
Catalyst supports
Hydrogen storage
Flexible electronics eg. OLEDs
Fuel cell electrodes
Drug release membrane
Actuators
Batteries
Separation membranes

Conclusions









- Carboxylate/amine terminated side-chains can be attached to nanofibres.
- The degree of covalent attachment can be controllably altered.
- Thus provide a template which can be further modififed to develop more sophisticated structures, for applications such as biosensing.

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