Functional materials based on photo-responsive ionogels

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A “Grand Challenge” posed for analytical chemistry is to develop a capability for sampling and monitoring air, water, and soil much more extensively and frequently than is now possible. Such goals will require improvements in sampling methodology and in techniques for remote measurements, as well as approaches that greatly lower per-sample and per-measurement costs. The community of analytical chemists that work on the methodology of field measurements perhaps should heed some of the approaches being pursued for bedside medical diagnostics. I’ll let the reader directly peruse other Challenges in the report.

Lastly, I’ll observe that the world is a big place, and so

Why? So events in the molecular world can be conveyed directly and instantly to the appropriate authorities. Prevent large scale contamination of environment.

Ubiquitous sensing: Internet-enable every measurement!

This vision can only become a reality utilizing Lab on a Chip technology.
Outline

• Current issues of sensing systems
  – Cost of ownership
  – Fluid handling using pumps and valves

• Opportunity for Functional Materials
  – Stimuli responsive materials
  – Synthesis and characterisation

• Integration of material into device for fluid handling

• Outlook
Reagent based Nutrient Analyser (Ammonia)

- Setup ca. 1999
- Worked well but not an integrated system

Phosphate Analyser Platform (Gen1)

- Electronics
- Fluidics
- Detection
- Comms
- Sampling
- Pumps & valves
- Chemistry
- Power
Next Generation device

- GEN2 developed; cost now ca. €250 per unit; launched at Environ 2010 (Feb)
- System still reliant
Cost Comparison of device (€)

- Smart engineering
- Smart materials

Gen1: [Cost Distribution]
Gen2: [Cost Distribution]
Future: [Cost Distribution]
Generation 3 system

- Current fluid handling components not suitable to miniaturised microfluidic systems- solenoid and electric motors for valves, actuators, pumps etc.

- Existing systems require large amount of power, space and expense.

- ‘Biomimetic’ approach to sensing and liquid handling based on intelligent materials.

- Realisation of futuristic sensing systems (3G model) lies within materials science

- Stimuli responsive materials for fluid handling
  - Electrochemical
  - Magnetic
  - Chemical
  - Optical

- Properties that can reversibly change e.g. chemical binding behaviour, surface charge/polarity, porosity, permeability, dimensions,.....
Photo-responsive materials based on spiropyran


- Optically actuate between two distinct isomers
- Control physico-chemical properties of system
- Non-contact spatial control of actuation
Multiple Personalities!

Solvatochromic

Metal ions, Proton, Protein and DNA recognition site

Thermochromic

Thermal relaxation dependent on all processes!

Absorbance (a.u.)

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Absorbance (a.u.)

Absorbance (a.u.)
Ionic Liquids- photoresponsive liquids

- Consist solely of ions and liquidus at RT
- Negligible vapour pressure, Non-flammable, thermally stable at high temperatures
- Designer solvents (viscosity, polarity, acidic, basic, electrochemical..) ability to tune ion composition
- Applications in catalysis, separations, polymerizations (ionic liquids in gels, solid state electrolytes)

Nano-structured liquids (Lopes et al 2008)

Photo-switching physicochemical interactions

Designer photochromics in ionic liquids

Polar and non-polar appendages locate molecule into specific regions

BSP 1 = R = (CH$_2$)$_2$OH
BSP 2 = R = (CH$_2$)$_3$CO$_2$H
BSP 3 = R = (CH$_2$)$_{13}$CH$_3$

Molecular modelling helps with design

Encapsulation of ILs- Ionogels

- Inorganic route (Li et al, 2004)
  - Oxides
  - Sol-gel
  - Applications in catalysis and photonics

- Organic route (Watanabe, 2004)
  - Polymers
  - Acrylamide gels
  - Applications in solid state electrolytes and separations

Combination of Ionogels and photo-responsive materials offers many advantages!!!!
Photo-responsive polymer

- Protonated isomer incorporated into cross linked thermoresponsive hydrogel
- Irradiation of blue light results in contraction of hydrogel
- Excellent spatial resolution demonstrated by micro-relief structures
- This offers the possibility of inducing dramatic changes to the bulk properties of a system by photonic irradiation.
- Technical issues include evaporation of water from hydrogel

**Chem. Mater., 19 (11), 2730 - 2732, 2007.**

Sumaru et al
Preparation of photo-responsive ionogel

Hydroxyl-Benzospiropyran + Acryl Chloride → Acryl ester benzospiropyran

1) Ionic Liquid
2) 365 nm Irradiation 10 mins
3) 1mM HCl

Ionogel

Byrne, Biosens & Bioelec, 2010 (accepted)
Photoresponsive ionogel valves

- Photo-polymerization takes place in ionic liquid matrix.
- Ionogels have different chemical and photo-physical properties due to ions with within the gel.

\[ X:Y:Z = 1:99:5 \]

Physical profile analysis
Rate constant = 0.457 s\(^{-1}\).

Multiple valves on one chip, using one actuation source!

Let the chemistry do the work!!

Grzybowski et al, JACS 2009 132, 1198.  
Conclusions

• Great potential for platforms capable of sophisticated multi-functional behaviour
  – Pumping
  – Valving
  – Predetermined delivery functions
  – Ionogel Biosensors (Caroline Barry Thursday 11.40am Symposium B)

• Materials must reliably perform functions comparable to conventional devices
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• Lest we forget
Thanks for listening!