Switchable Materials- The Route to Next Generation Multifunctional Analytical Platforms

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Tetraester & Tetraphosphine Oxide

Calix[4]arene Tetraester [Na$^+$]

Calix[4]arene Tetrakisphosphine oxide [Ca$^{2+}$]
PVC - Membrane ISEs

Typical membrane cocktail (%w/w); PVC:33%, NPOE (plasticiser): 66%; ionophore/exchanger: 1% (ratio at least 2:1 by mole); dissolve in a volatile solvent e.g. THF and cast membrane from this solution.
Molecular Functionality

*TME:Na+ Side-on View*

**Fig. 3.** Comparison of plasma sodium analysis using the array-FIA approach with a SMAC analyser. Good correlation without bias is obtained [5].

Ligand (and variations of) are used in many clinical analysers for blood sodium profiling.

response of TPOL electrode

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tr>
<td>Synonyms</td>
<td>4-tert-Butylcalix[4]arene-tetraacetic acid tetraethyl ester</td>
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<td>Molecular Formula</td>
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<td>S: 22-24/25</td>
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<td>Literature References</td>
<td>Ionophore employed in solid-state and polymeric membrane sodium-selective electrodes. D. Diamond et al., Anal. Chem. 64, 2496 (1992)</td>
</tr>
</tbody>
</table>

**Miscellaneous:** Ionophores (potentiometric) for ion-selective electrodes

Fame at last!!

Best ionophore for sodium
Fame at Last!
Keynote Article: August 2004, Analytical Chemistry (ACS)


Dermot Diamond
Dublin City University
(Ireland)

Incredible advances in digital communications and computer power have profoundly changed our lives. One chemist shares his vision of the role of analytical science in the next communications revolution.

Digital communications networks are at the heart of modern society. The digitization of communications, the development of the Internet, and the availability of relatively inexpensive yet powerful mobile computing technologies have established a global communications network capable of linking billions of people, places, and objects. Email can instantly transmit complex documents to multiple remote locations, and websites provide a permanent, unambiguous representation, dissemination, and exchange of information globally. This technology is now pervasive, and those in research and business must make interactions with the digital world every day. However, this technology might simply be the foundation for the next wave of developments that will provide a seamless interface between the real and digital worlds.

The crucial missing part in this scenario is the gateway through which these worlds will communicate. How can the digital world sense and respond to changes in the real world? Analytical sensors—particularly those working on chemical sensors, biosensors, and compact, autonomous instruments—are...
Fundamental Problem: Sensor surface will change with time!

Surface interactions are critical to signal generation - very susceptible to any process that modifies the surface condition => drift, loss of sensitivity => regular calibration => high cost of ownership

- Leaching, biofouling, physical damage, sample interferents, ..... 
- Engineers expect a thermistor, we have platforms closer to a washing machine!
Direct Sensing vs. Reagent Based LOAC

**Direct Sensing**
- Outside world
- Sensor
- Sample
- Signal
- Molecular interactions

**LOAC Analyser**
- Sample
- Reagent
- Source
- Reaction manifold
- Detector
- Waste
- BL
- Blank
- t
- s
Adaptive (Stimulus-Responsive) Materials

- Materials that possess ‘multiple personalities’ or characteristics
- Can switch reversibly between these via a stimulus (chemical, electrochemical, photochemical.....)
- Properties change dramatically e.g. chemical binding behaviour, surface charge/polarity, porosity, permeability, dimensions, colour.....
Switchable Materials: Soft Polymer Actuators

Principle can be used to make soft polymer (biomimetic, artificial muscle) actuators such as ‘benders’

(multi-laminated structures designed so that an outer PPy layer expands as the inner contracts to produce a bending movement)
‘Artificial Muscle’ - Mobile Platforms

- Conducting polymer fibre bundles contained within polymer ‘skin’
- Mobile electrolyte solution
- Polarisation of the bundles causes movement of ions and associated water molecules due to charge compensation
- Causes swelling or contraction
- Effect can be translated into bending by laminating two oppositely polarised layers with a flexible porous inactive intermediate layer - soft pumps and valves!

Videos from Moshen Shahinpoor’s website at www.unm.edu/~amri
Polymer Micropumps and Valves

- Low power, low cost components are vital for realisation of next generation micro-dimensioned analytical platforms
- Based on polypyrrole CP ‘benders’
- Soft polymer actuators more attractive for integrated ufluidics manifolds
- ‘lego’ approach - detector block will slot in

Daniel Kim and Kim Lau
Soft Polymer Actuators

- Can be used to provide pumping and valving functions
- Can be fully integrated into microfluidic manifolds
- In principle are more reliable in microscale than conventional ‘hard’ materials
- Could drive down the cost and complexity of ‘analyser’ platforms
Photoswitchable Materials

[Diagram of chemical structures showing UV/Vis transition between two states]

Absorbance (ABS) vs. Wavelength (NM) graph showing two states:
- Off (spiropyran)
- On (merocyanine)

This work is supported by Science Foundation Ireland under grant 07/CE/I1147
Various diamino alkyl linkers

Each –CH₂- link is ca. 1.5 Å

Can be immobilised on polymer or silica surfaces, or within bulk materials, e.g. using SP-modified monomers

<table>
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<tr>
<th>Tether Length (n=)</th>
<th>ID</th>
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<tr>
<td>2</td>
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<tr>
<td>4</td>
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<td>6</td>
<td>SP-6</td>
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<td>8</td>
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Importance of Linker Length

SP-MC Switching

Co\textsuperscript{2+}-Complexation

![Graphs showing absorption as a function of wavelength for different linkers and Co\textsuperscript{2+}-complexation](image)

- Passive (closed)
- Active (open)
- Complexed

This work is supported by Science Foundation Ireland under grant 07/CE/I1147
Detection of switching between SP/MC/MC-Cu$^{2+}$ states using the ‘Discophotometer’

Absorbance measured at 560 nm for cyclical switching between SP and MC when for surface immobilized (full circles) and non-immobilized (open circles) SP-1.


Merocyanine Interaction with Amino Acids

A strongly coloured solution of merocyanine and tyrosine in a 4:1 acetonitrile:water mixture. The merocyanine was formed by illuminating spiropyran (1:1 mole ratio to tyrosine) for 1 minute with a UV-LED. The picture was taken after 100 hours storage in the absence of light. (top, right): The control experiment without tyrosine shows almost complete decoloration, i.e. return to spiropyran form.

Energy minimised structures (Chem 3-D Ultra, V. 9.0, Cambridgesoft) suggests complementary binding of tyrosine to the merocyanine zwitterion which stabilises the coloured merocyanine form.

Key: carbon atoms – grey, oxygen atoms – red, nitrogen atoms – blue (hydrogen atoms not shown for clarity)

Photocontrolled DNA Binding

Photoswitched DNA-Binding of a Photochromic Spiropyran

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Figure 1. Absorption spectra of 1c (top panel) and 1o (lower panel) in the absence (blue lines) and presence (red lines) of calf-thymus DNA. The contribution from DNA to the overall absorption has been subtracted for ease of comparison. Likewise, the contribution from 1c has been subtracted from the spectra of 1o shown in the lower panel. The green line corresponds to a sample of 100% 1o bound to DNA as the contribution from unbound 1o has been corrected for (see Supporting Information for details). The total concentration of 1 was ∼1.5 × 10⁻⁵ M. The concentration of DNA was 11.6 × 10⁻⁵ M, and the NaCl concentration of the solution was 8.6 × 10⁻³ M.

Chart 1. Structures of Photochromic Spiropyran 1
Functionalised Microbeads: optically controlled selective binding of metal ions

Changing EOF in CE using Light!

Optical microscope images of poly (spiropyran-co-divinylbenzene) monoliths in both the spiropyran (A) and merocyanine (B) forms.

Scanning electron micrograph of the monolithic poly (spiropyran-co-divinylbenzene) within the PTFE coated fused silica capillary; channel dimensions 8mm x 0.4mm x 0.4mm

Polymer based photoactuators

Figure 3. (a, b) Images of the pSPNIPAAm hydrogel layer just after the micropatterned light irradiation. Duration of irradiation was (●, red) 0, (○) 1, and (■, green) 3 s. (c) Height change of the hydrogel layer in (●) non-irradiated and (○) irradiated region as a function of time after 3 s blue light irradiation.

Polymer developed by by Kimio Sumaru et al\textsuperscript{1}

Photo-actuator polymers as microvalves in microfluidic systems

trihexyltetradecylphosphonium dicyanoamide
[P6,6,6,14][dca]
Mobile platforms with chemical actuation: No external power required

Based on solvent exchange within ionogel (water/ethanol)

Robert Byrne and Fernando Lopez
Conclusions

- Switchable materials open the way to devices with radically different behaviour - much of which can be applied to analytical flow systems
  - Biomimetic polymer pumps and valves
  - Photocontrolled actuation
  - Photocontrolled uptake and release
  - Movement of loaded particles and structures
  - Very low power flow systems
- .......

Very exciting possibilities for developing next generation analytical devices including separations targeting many environmental and pHealth applications