Current, Emerging and Future Technologies for Sensing the Environment

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Abstract

This paper reviews current technologies that are used for environmental monitoring, and presents emerging technologies that will dramatically improve our ability to obtain spatially distributed, real-time data about key indicators of environmental quality at specific locations. Futuristic approaches to environmental monitoring that employ fundamental breakthroughs in materials science to revolutionise the way we monitor our environment will also be considered. In particular, approaches employing biomimetic and 'adaptive'/'stimuli-responsive' materials will be highlighted, as these could play an important role in the realization of small, low power, low cost, autonomous sensing and communications platforms that could form the building blocks of the much vaunted environmental 'sensor web'.

Introduction

Around the world, the ability to monitor environmental status is now a priority for many countries. The prioritisation of environmental monitoring has been driven by a number of factors including climate change, recognition of the importance of the environment for sustainable economics, linking of environmental monitoring with threat detection and the implementation of an array of European Union environmental directives by Member States. The ability to accurately determine 'environmental status' is the prerequisite for quantifying environmental change, or for detecting pollution events in their early stages. Without this ability, it is impossible to implement policies aimed at improving the status of our environment, and the potential to waste enormous resources by Governments through ineffective or misguided policies is very real. There also is a need to define what we mean by environmental status, and whether this status is 'good' or 'bad', or whether the status is changing. For example, key indicators must be identified and tracked, both spatially and temporally, and status windows defined to enable 'within specification' or 'out of specification' conditions to be detected. When implemented at 'internet-scale' globally, this gives rise to the concept of the 'environmental nervous system' – a system that constantly monitors the status of our environment and can respond rapidly to sensed events through complex feedback loops to specialists, communities, individuals, control actuators etc.

This concept is clearly massive in scale, and its implementation requires many sensing modalities to be harnessed collectively in order to access the required analytical information. The term 'internet-scale' is appropriate as, in a way, what needs to be delivered is a sensor web, that is intimately woven into the existing internet, continuously gathering, filtering and interpreting sensed information relevant to the environment, detecting unusual patterns, classifying events, locating geographical locations and dynamics of these events, and ideally, predicting events and organising appropriate action in advance of any major environmental damage.

Now, the scale of this vision is truly enormous, and its realisation is still well beyond the current state-of-the-art. Perhaps the best-developed means of doing global scale sensing of environmental parameters is through satellite imaging. In recent years, the employment of specific spectroscopic probes for key target gases in the atmosphere has augmented the familiar weather information related to pressure fluctuations, temperature, cloud cover and rainfall activity. The coupling of widely distributed geographical coverage with specific molecular information enables the distribution of chemical targets to be monitored and variations mapped as a function of location and time. These fluctuations can be linked further to specific activities (e.g. to identify the source(s)) and to weather conditions (e.g. to understand the dynamics). Figure 1 shows the geographical distribution of averaged NO2 levels over Ireland and part of Britain measured by the SCIAMACHY instrument on the Envisat satellite during April 2008. SCIAMACHY is an imaging spectrometer whose primary mission objective is to perform global measurements of trace gases in the troposphere and in the stratosphere [1]. During these measurements, the atmospheric column directly under the satellite is observed, with each scan covering an area on the ground of up to 960 km across the satellite track with a maximum resolution of 26 km x 15 km. The data, presented to the user as GIS coordinates with an accompanying NO2 concentration value (in molecules per cm2), is imported into a 3-d visualisation program which is used to generate a colour contour plot and the resulting image mapped onto the appropriate region.

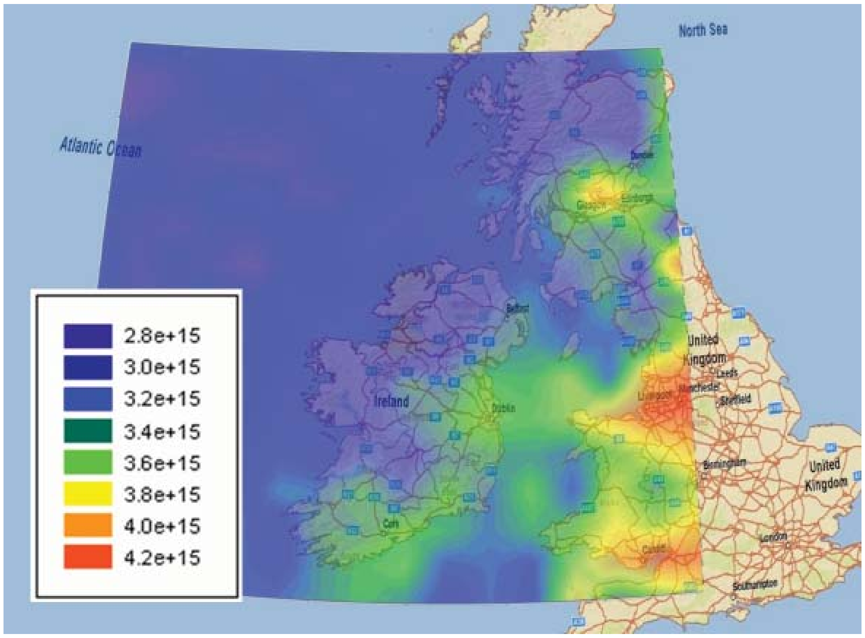

Figure 1. Average atmospheric levels of NO2 over Ireland/UK during April 2008 measured by the SCIAMACHY instrument on the Envisat satellite. In this example the atmospheric volume directly under the satellite is observed. Each scan covers an area on the ground of up to 960 km across track with a maximum resolution of 26 km x 15 km. The NO2 concentration scale unit is in molecules per cm2. The concentration distribution image is generated by importing the European Space Agency data into Sigmaplot and generating a semi-transparent colour contour plot, which is then superimposed on the area map.

From Figure 1 it can be concluded that elevated levels of NO2 are associated with heavily industrialised areas in the UK around South Wales and the Midlands, and Glasgow in Scotland. In contrast, levels in Ireland are in general much lower, although there is evidence of higher levels around Dublin and on the east and south coasts. Similar approaches have been used to track SO2 plumes originating from Mount Etna (Sicily) moving across Italy to Greece and Turkey, following a series of eruptions in May 2008 [2]. Satellite imaging can also be used to track the general quality of large water bodies. For example, Figure 2 shows the distribution of algal blooms off the west coast of Ireland in 2006 [3].

Clearly satellite-based imaging techniques can provide very useful information that can enable certain aspects of air and water quality to be monitored dynamically over large geographical areas. The ideal situation would be to augment the satellite-based information with data obtained from widely distributed surface deployed sensors, as through the latter we can obtain very specific and precise information about air and water chemistry/biology at particular locations. Hence, chemo/biosensors provide very complementary information to that obtained via satellite measurements. What is needed, therefore, are chemo/biosensors deployed in massive numbers at multiple locations, i.e. internet-scale environmental sensor web [4]. If follows, therefore, that massive scale-up in terms of the numbers of deployed sensors must happen, and these must be capable of integrating into existing communications infrastructure. However, massive scale-up implies that the cost base of the basic sensor/communications building blocks (sometimes referred to as sensor motes/nodes [5]) must be very low, and indefinitely self-sustaining [6].

Current Approaches and Emerging Technologies

From the above discussion, the ideal scenario for the realisation of a functioning environmental nervous system based on collaborative information harvesting from satellites and from extensive ground-based sensor network deployments. The problem is that the chemo/bio-sensor networks do not exist. The reason is simple but very difficult to overcome. The cost of ownership in terms of initial capital outlay and ongoing running costs is far too high. This, in turn, arises from the relatively complex mode of operation of these devices, compared to their better behaved and lower cost physical sensor cousins (thermistors, piezo-vibration sensors, light intensity detectors, etc.). Generally speaking, chemo/bio-sensors employ some kind of molecular recognition event (enzyme-substrate, ligand-ion), which is coupled with a transduction mechanism to generate (ideally) a molecule-specific signal that can be detected. Typically, these molecular recognition agents are immobilised on a surface or within a membrane that is housed in some type of sensor head or probe that is exposed to the sample. The sensor's task when immersed in the sample environment is to provide information about the chemical or biological composition of the sample through these tailored molecular binding events. The problem is that the sensor surface must therefore be 'active' in that these binding events must occur, and the sensitive molecular binding sites must be intimately exposed to the sample, which more often than not contains many components that can interfere or passivate this active surface. Therefore, it is not surprising that in order to function properly, chemo/biosensors need regular calibration and cleaning/servicing, which drives up the cost and complexity of these devices, and making large-scale deployments prohibitively expensive and difficult. For example, chemical analysers cost in the region of €5K-€50K, depending on the types of measurements being made [7].

It is understandable, therefore, that most chemical and biological water quality measurements still involve taking samples manually which are analysed subsequently at centralised laboratory facilities using very sophisticated bench-top analytical instruments. One way to tackle this issue of how to maintain acceptable analytical performance with field-deployable systems is to employ microfluidic manifolds through which manual operations like sampling, sample processing, analytical measurement, and calibration can be integrated. These manifolds, when further integrated with electronics, fluid handling, and wireless communications, provide a route towards high performance, field deployable analytical instruments with a more acceptable cost base (€500-€5,000). For example, Figure 2 shows an instrument we have developed for the field deployment of nutrients such as phosphate in natural waters. The analyser is based on colorimetric methods that employ a reagent that reacts selectively with a target species (in this case, the yellow method for phosphate detection), with the resulting colour being detected using a low cost, low power LED-photodiode system [8,9,10]. The analyser performs 2-point calibrations (0 mg/l and 10 mg/l phosphate) at user-defined intervals, and can be left in-situ for several months unattended. Power is provided by an integrated lead-acid battery which can be augmented by a solar panel if required.

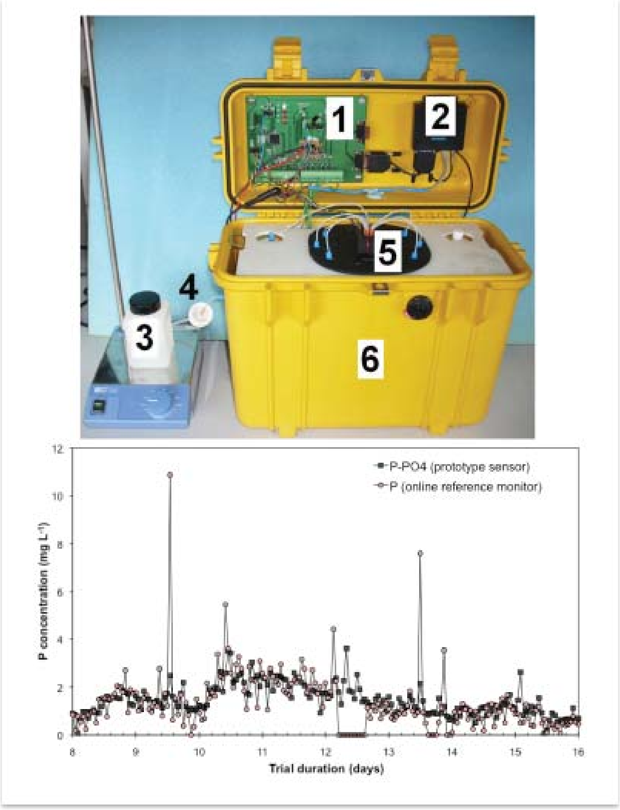

Figure 2. Top - the phosphate analyser during a typical laboratory trial. (1) Control board and data storage (2) GSM modem for transmitting data (3) Sample container (4) Sample filter (5) Microfluidic chip / detector assembly (6) Ruggedised container with storage space for reagent, calibration solutions, waste and power supply (12 V lead-acid battery). This is typical of the current form factor of analytical instruments designed for remote autonomous deployment in environmental monitoring situations.

Figure 2. Bottom - typical results generated during part of a 44-day trial at a waste-water plant. The prototype system data (squares) in general are in excellent correlation with the commercial reference system (circles), and the phosphate levels are typically below 4 mg mL-1. High levels recorded with the reference system at ca. 9.6 days and 13.5 days are correlated with the presence of solid waste in the samples, which is filtered out by out prototype system but not by the commercial system. The baseline signals at ca. 12.2-12.6 days and around 13.6-14.0 days coincided with the reference system being down for servicing.

The data shown are a subset of results generated during a 44-day trial during June-August 2008 at a wastewater treatment plant (days 8-16 shown). Some features are immediately apparent; for example, the data is generally in excellent agreement with the plant's existing on-line monitoring reference system (Aztec P100, Capital Controls, UK), showing that the prototype analyser is capable of generating accurate analytical data. The analyser is completely autonomous, and in this particular trial, measured the phosphate level on an hourly basis, transmitting the data using SMS text messaging every 5-hours. There are occasion issues with bubbles that cause spikes in the prototype system detector output, but these can be easily filtered out from real analytical data using appropriate software algorithms. Also, spikes appear in the reference system due to solids that are digested within the instrument and add to the phosphate concentration, whereas these are physically filtered out in the prototype analyser.

Futuristic Approaches – The Role of Nanomaterials

Using similar approaches we have also built and field trialled autonomous systems for analysing greenhouse gas emissions from landfill sites (using IR sensors for CH4 and CO2) and for monitoring dust is air based on a portable XRF detector and in-house developed dust sampling unit (to detect a range of toxic metals). However, these platforms, while useful advances on available technology, are still too expensive and conventional to bring to 'internet scale' in terms of deployments. The price performance index still needs to be driven down by orders of magnitude, and this will require truly innovative thinking and fundamental breakthroughs that can only emerge from basic materials science. One approach we have been focusing on for the past few years is the development of materials that can switch between radically different sets of characteristics. This 'switchable' behaviour can extend across differences in colour, polarity, porosity, permeability, physical dimensions (expand, contract), chemical activity (active, inactive), and so on. Switching can be triggered using light, electrochemical potential, or local chemistry (e.g. pH). The motivation underlying this research effort is the realisation that next generation analytical platforms and sensors need to be much more sophisticated than existing devices, and this sophistication will emerge through control of materials behaviour at the molecular level. Two material types we have been focusing on are conducting polymers and photo-responsive 'spiro'-type compounds.

With the conducting polymers, we have focused to a large extent on producing building blocks of next generation fluidic platforms that incorporate soft polymer actuators as the active basis for pumps and valves that are biomimetic in nature, rather than the conventional engineered micro-components employed in most microfluidics research. In contrast to these conventional components, soft-polymer actuators are low power, and less prone to malfunction due to particulate ingress. Figure 3 shows two subunits we have developed, a switchable mesh-valve structure [11] and a biomimetic polymer pump [12,13]. Integration of structures like these into circulation systems could lead to new fluidic platforms that are reliable, low-cost, and fully compatible with small, compact design formats. The incorporation of simple circulatory systems in analytical instruments is an attractive approach to adopt, as it enables more flexibility in terms of sensing strategy. Conventional chemo/bio-sensors tend to employ sensitive surfaces or membranes that have specific molecular receptors immobilised in such a way that they interact with the sample and generate a signal. Unfortunately, these surfaces, being active in nature (as they must interact with the sample at the molecular level), begin to change immediately on exposure to the real world. For example, the binding sites may become occupied or rendered inactive by fouling or strong interactions with sample components other that the species of interest. This gives rise to drift and loss of response sensitivity, and regular calibration is therefore a primary requirement if the sensor data is to be reliable.

In remote locations, this in turn means that the instrument must include all reagents and standards required to maintain the sensor within calibration. Pumps and valves drive up the price and power demand and limit scalability. Hence biomimetic approaches to fluid handling could simultaneously keep cost and complexity down, while still enabling the instruments to be calibrated. Furthermore, if chemo/bio-sensors are employed to generate the signal, they can be housed within the microfluidic platform rather than being exposed to the real world, which can help extend lifetime. Alternatively, reagent based approaches can be employed, as in the case of the phosphate instrument mentioned above, which opens up methods and approaches that are not possible using probe-type devices that are directly exposed to the sample.

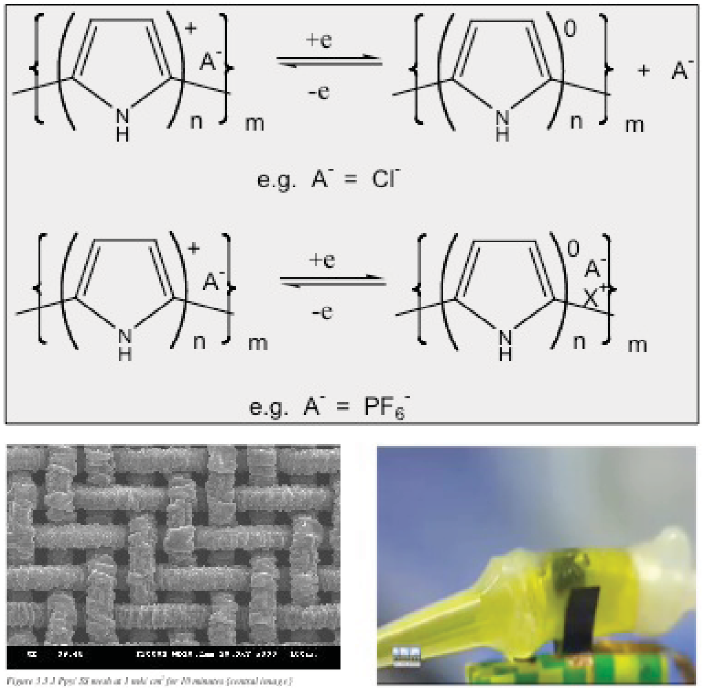

Figure 3. Top – polypyrrole can be reversibly switched between oxidised (positive) and reduced (neutral) forms by addition/removal of electrons. To maintain charge neutrality, ions move into/out of the polymer. This dramatic change in the local electrostatic environment is accompanied

by movement of associated water of hydration in/out of the polymer. Overall this results in swelling/contraction of polymer.

Middle (left) – Polypyrrole deposited on a stainless steel mesh substrate with a pore size ca. 20 μm, with the pore size dependent on the underlying mesh dimensions and the amount of polymer deposited. Switching the polymer through its redox cycle makes the average pore size expand and contract, which in turn enables the flow rate through the mesh to be controlled. Control of the nanostructure of the polymer (e.g. through modification of the monomer structure and polymerisation process) coupled with control of micro-scale structure (e.g. through the substrate configuration) is vital for tuning the behaviour of the bulk material.

Middle (right) – a biomimetic pump based on polymer actuator 'benders'. These are constructed by laminating two polymer strips with an intermediate insulating, flexible porous layer and configuring the two polymer strips to actuate in opposite manner (one expands when the other contracts) to produce a bending effect. In this case, the effect is used to drive liquid from a chamber. Cycling through the polymer redox states results in a pumping effect reminiscent of a heart. Improvements in the efficiency of such structures requires a fundamental knowledge of the molecular basis of the mechanisms underpinning the macro-scale device.

While microfluidics and 'lab-on-a-chip' systems are a very attractive route to realising some degree of scale-up for distributed environmental monitoring, they still suffer from some inherent limitations. For example, reagents and standards will eventually be consumed or degraded, and devices will have to be replaced or serviced, even though scaling down the fluidic system results in dramatic reductions in the volume of reagents required for extended periods of operation [14,15].

A radically different approach to the use of highly calibrated sensors is to deploy large numbers of very simple sensors without calibration and to use the response patterns generated to cross-validate decisions. Figure 4 shows fabrication details and responses obtained with a very low cost gas sensor based on LEDs. The chemical response function is obtained by coating the LEDs with a film incorporating a chemo-responsive dye (in this case bromophenol blue immobilised in ethyl cellulose). The sensor and associated electronics have been integrated with a low-cost wireless communications circuit to produce a gas sensor node costing ca. €10. Despite its simplicity, this device has surprisingly good response characteristics, with the LOD for acetic acid in the mid-ppb range, excellent dynamic response (seconds) and reproducibility. We have used clusters of these simple sensors to detect not only that an acid plume has been released, but also to identify the likely source, and estimate the dynamics of plume movement [16].

However, these sensors employ relatively well-known and simple sensing approaches based on chemo-responsive dyes that have been known for decades. More recently, we have begun to work with dyes that can be switched between an inactive (non-binding) form and an active (binding) form using light [17,18]. For example, spriropyran derivatives can be reversibly switched between the spiro (SP) form which is chemically inactive, and an active merocyanine (MC) form which is chemically active, using UV and white/green light, respectively (see Figure 5). Furthermore, the system is inherently indicating, as MC is strongly coloured (purple) while SP is colourless. The MC form is also strongly charged (zwitterionic) while the SP form is

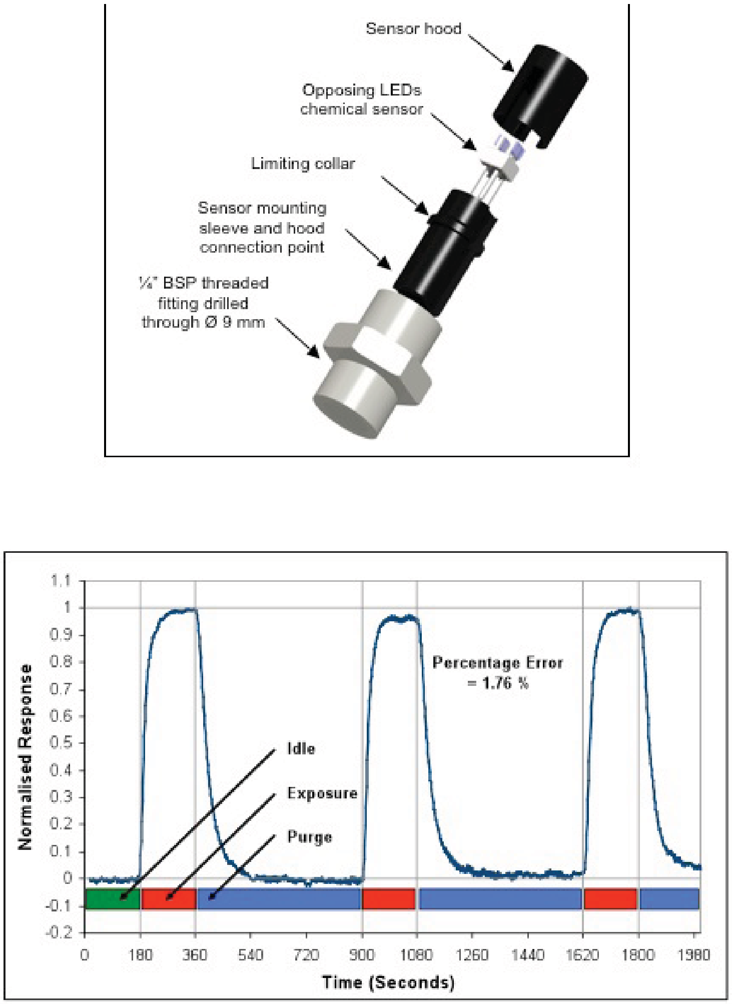

Figure 4. Top: Fabrication details for low-cost gas sensor based on LEDs coated with a film incorporating a chemo-responsive dye. Exposure to an acidic plume causes the dye colour to change which modulates the light flux between the LED emitter and a reverse-biased LED detector. The light flux is monitored by the time taken to photo-discharge a set voltage on the reverse biased LED. A critical challenge with such devices is the need to produce batches with more-or-less identical response characteristics (to reduce the need to calibrate). This in turn requires ****

Bottom: Response of the coated LED chemical sensor node to three consecutive exposures of 1 mg/l acetic acid vapour. Note the very rapid response and recovery, and excellent sensitivity and reproducibility.

uncharged. The MC form has been shown to bind certain metal ions and interact with amino acids [19], with the binding also indicated by new absorbance bands in the visible region. The binding can also be reversed using light, with white or green light causing the guest species to be expelled and the inactive SP form to be regenerated.

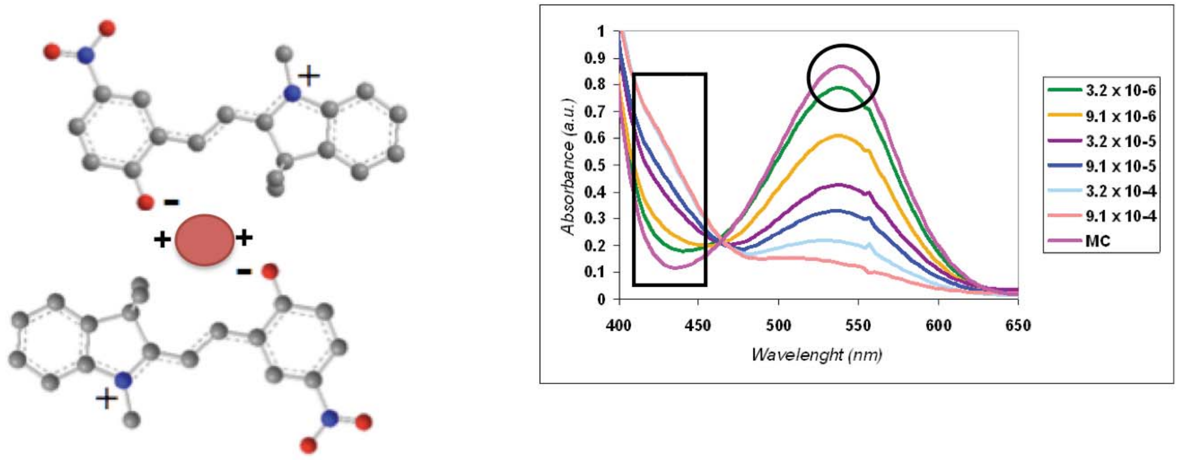

Figure 5. Left: Merocyanine forms a 2:1 sandwich-like complex with certain metal ions like Cu2+ and Co2+, but the spiropyran form is inactive and does not interact with the metal ions.

Right: Spectral changes accompanying Cu2+ binding by merocyanine. The strong MC absorbance (λmaxca. 540 nm) reduces in intensity and a new band associated with the complex simultaneously appears in the region 400-440 nm, with an isosbestic point at ca. 460 nm. Tuning of this behaviour requires careful optimisation of the surface nanostructure, and in particular, the tether length of the binding sites from the surface.

For sensor researchers, systems like SP-MC offer intriguing possibilities for the development of relatively simple sensing devices that nonetheless could possess sophisticated characteristics. For example, the sensing surface could be held in a passive form until a measurement is required. An external stimulus (UV light in this case) is used to generate the active form, which interacts with the sample, generating the signal in the process. Upon completion of the measurement, an external stimulus is used to expel the bound molecules from the surface, and regenerate the passive form (white or green light in this case). As each state has a different absorbance spectrum in the visible region, it can also report its status to the external world (i.e. whether it is in the active-free, active-bound, or passive states). We have shown that drift can be easily distinguished from a genuine response by monitoring the film's colour using clusters of LEDs, enabling a degree of self-diagnostics to be built into the measurements [20].

Conclusions

It is likely that in the near future, combinations of relatively simple sensors like these with more sophisticated calibrated devices will be deployed to provide a much more information-rich environmental monitoring capability than is currently available. This, coupled with satellite measurements, will enable our environment to be monitored dynamically on a global scale. However, if the visions of 'internet-scale sensing' and the 'environmental nervous system' are to be truly realised, it will require a well-coordinated, multidisciplinary global research effort that encourages linkages between established teams through multi-national programmes sponsored by agencies.

It also must integrate much more effectively research in fundamental materials science, analytical/sensor science, environmental science, instrumentation engineering, and satellite imaging, and bring together academic, governmental and industry research teams in a combined effort to drive the science and technology of distributed environmental monitoring forward. The pieces are already in place – now it is time to bring them together, and, as we know from thermodynamics, this will require effort and energy if it is to happen!

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