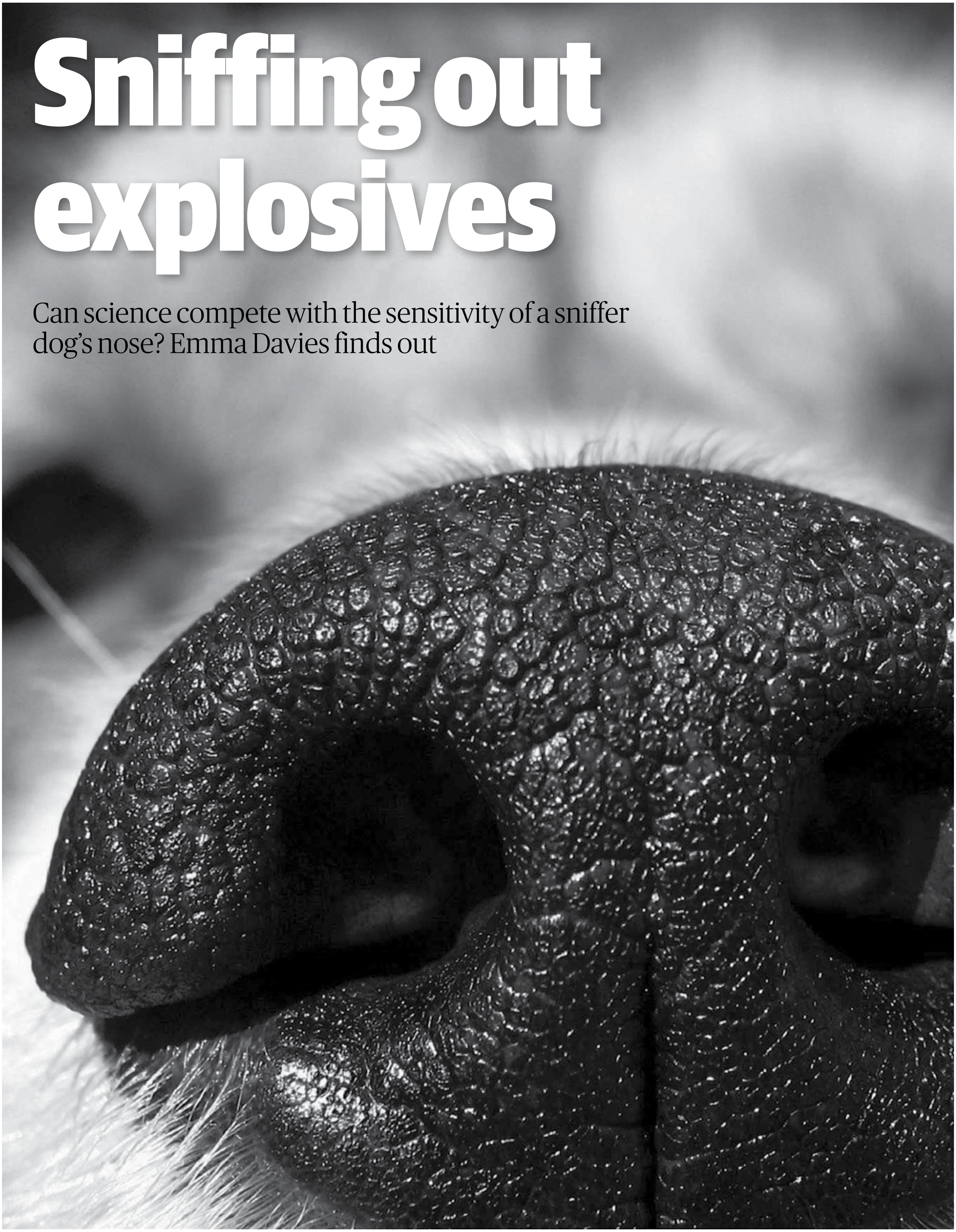
Sniffing out explosives

Can science compete with the sensitivity of a sniffer dog's nose? Emma Davies finds out



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The aptly-named Fido handheld device can detect explosives vapours at levels that almost match a sniffer dog's nose

Timothy Swager often finds his mind drifting back to the 7 July 2005 bombings. The Massachusetts Institute of Technology (MIT) chemist was on sabbatical in London at the time. 'There's one thing I think about a lot. Those guys with the backpacks would have been easily detected with some chemical sensors,' he says. 'Starting back at Luton when they went through a door into the train station wearing backpacks giving off vapours, you could have had some very small, inexpensive sensors over the top of the doors that would have said: there are people to watch here.' One sensor could give too many false alarms but a series of sensors at different spots in the train station would be able to pick up the same people again and again, he adds.

Swager is famed for creating polymer technology to sniff out explosives vapours in the field, commercialised as Fido explosives detectors. The arrays of unobtrusive sensors that he envisages may not be that far from reality. Researchers can already detect single molecules of explosives using sensing systems that have the potential to be cheap, low-power and very, very small – thanks to some clever chemistry and consumer-driven miniaturisation of electronics. Most of these vapour detection systems are designed to identify molecules of high explosives such as TNT (2,4,6-trinitrotoluene).

Good dog

The nose of a sniffer dog is still the best detection system for explosives, but technology is creeping ever closer to matching its sensitivity. The aptly-named Fido explosives detector that emerged from Swager's lab has been through a series of incarnations. It is now sold by Flir Systems in the US, as a range of small handheld devices used widely by US troops. These detectors can spot explosives vapours at concentrations of parts per quadrillion (1 in 10^{15}), comparable to the sensitivity of a dog's nose.

For his original technology, Swager used thin films of fluorescent semiconductor polymers which absorb UV or blue light and re-emit it as fluorescence. Aimee Rose is a product manager at Flir Systems and began her PhD with Swager in the late 1990s, when the technology was in its infancy. 'At the time it was very difficult to use fluorescent polymers in the solid state. People would dilute them down to very high levels but that would impact sensitivity,' she recalls. 'Tim [Swager] invented one of the first fluorescent polymers that actually maintains fluorescence when you make a thin film out of it instead of having it in solution.' The fluorescence turns off in the presence of nitroaromatic compounds, such as TNT, because the photoexcited polymer is more likely to transfer an electron to the electronegative TNT molecule than to emit light. Each TNT molecule can stop the light emission from a large number of surrounding polymer molecules.

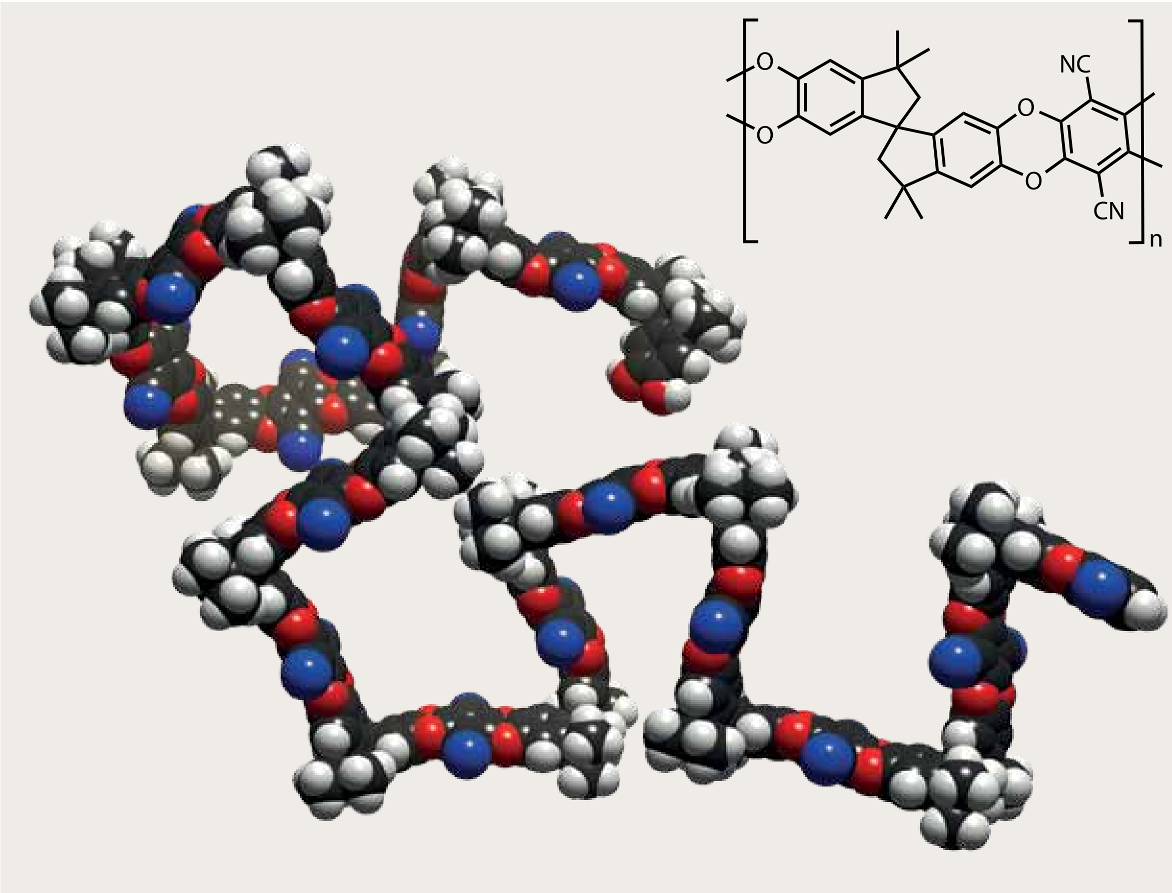
Flir Systems has recently made a prototype multi-channel device to sense up to eight different explosives vapours at once. The device contains polymer 'tapes' that can be changed depending on what you are looking to detect. 'At the chemical level we can design fluorescent materials to respond to a specific analyte,' says Rose. The company is currently focusing on explosives detection, but a different set of tapes could conceivably be designed to detect chemical weapons, she adds.

Shrinking down

In the Organic Semiconductor Centre at the University of St Andrews, UK, Graham Turnbull and Ifor Samuel have been working on explosives detection systems that are loosely based on the Fido technology. But rather than using fluorescence to detect explosives, they focus on using laser light from fluorescent polymers in a bid to create miniature yet sensitive devices.

The St Andrews researchers have created a series of miniature organic semiconductor lasers made from thin films of blue light-emitting polyfluorene and other polymers.

When excited by a pulsed light source, the fluorescence emitted inside the polymer film is amplified. The films are made with a corrugated surface which then reflects this amplified light back and forth to create a directional beam of laser light, unlike



NEIL MCKEOWN/CARDIFF UNIVERSITY

Using rigid, contorted fluorescent polymers gives a porous film, which vapours can penetrate, improving sensitivity

fluorescent light which is emitted in all directions. Vapours from explosives increase the pulsed light power needed for the laser to switch on, and also cut the efficiency of laser light generation to give a large change in output power. 'These materials work very well as a sensitive and fast detector of explosives,' says Turnbull. In lab tests, exposing a polyfluorene laser to less than 10ppb of the test molecule dinitrobenzene dimmed the laser light in seconds, in what is a reversible process. The Scottish researchers are currently working on a prototype detector.

These polymer lasers can be powered solely by pulsed blue LEDs, which could lead to very simple, lightweight, and miniature explosives detectors. The researchers are partners in an EPSRC (Engineering and Physical Sciences Research Council) project called Hypix, which aims to create miniature devices where plastic lasers are powered by a layer of blue LEDS, mounted on and controlled by silicon computer chips. One aim of the project is to develop systems for visible light communications – imagine a ceiling LED that sends out wireless data to your gadgets – but the same technology has also been used to create on-chip fluorescence sensors for explosives vapours.

'We can design fluorescent materials at the chemical level to respond to a specific analyte'

Together with chemist Neil McKeown at the UK's Cardiff University, Turnbull and Samuel are also working on another type of fluorescent sensor containing microporous polymers. 'The polymers have a very contorted structure that leads to pores close to a nanometre in size throughout the polymer film,' explains Turnbull.

Because light emission comes from the full depth of a fluorescent polymer, TNT molecules need to be able to penetrate deep into the film to switch it off. The pores allow molecules in explosives vapour to infiltrate polymer films more rapidly, giving a faster response. 'We see significantly larger and faster changes in the microporous materials,' Turnbull says.

Tubular bells

Single-walled carbon nanotubes (SWNTs), hollow one-atom-thick cylinders, could also make good explosives sensors, thanks to their fluorescence in the near infrared. SWNTs can be coupled to molecules designed to bind to a target molecule, so that the fluorescence changes in a measurable way when the target binds. Michael Strano at MIT is a pioneer in this field. His group has developed carbon nanotube sensors for a range of molecules from nitric oxide to hydrogen peroxide.

In the search for molecules that could impart the desired selectivity to the SWNTs, Strano came across a series of peptides in bee venom called bombolitins. 'These peptides will adsorb to the nanotube surface and recognise nitroaromatics,' says Strano. When bound, the nitroaromatics cause a shift in the fluorescence emission wavelength. The experiments are carried out in solution at present.

To monitor the binding, Strano's team built a fluorescence microscope that takes light from a sample and projects it onto a detector. The detector is divided into two sections and the fluorescent light coming from the nanotube is split, so that only half of the peak appears in each channel of the detector. When a molecule binds and causes a shift in wavelength, more light is projected onto one side of the camera than the other. 'We were actually able to show that we could detect single explosive molecules adsorbing onto a single carbon nanotube, which was an unprecedented feat,' says Strano.

Changing the SWNT diameter gives a different response. 'Each SWNT [size] emits at a different wavelength so we have the ability to look at 20 different nanotube sensors with the same peptide,' he explains. Changing the bombolitin will also give a different response. Strano suggests that the technology could be used to identify a 'fingerprint' for a specific explosive by using an array of nanotubes that each have a slightly different response to a molecule.

Swager has worked with Strano in the past on nanotube sensing systems. His current focus in this area is on using the nanotubes to create chemoresistors, which show a change in electrical resistance when analytes bind.

His team has successfully tested these devices on dimethyl methylphosphonate, which has similar hydrogen bonding characteristics and vapour pressure to chemical warfare agents. They are currently working on covalently modified multi-walled carbon nanotubes to detect volatile organic chemicals such as explosives. Functionalisation is limited to the wall of the outer nanotube wall so the inner tubes continue to be highly conductive, increasing sensitivity.

Swager believes that the nanotube chemoresistors have the potential to be incorporated into very simple, low-cost devices, which would require minimal power. 'That's our goal,' he says. He can imagine these devices could be used for security at events such as the Olympics, with the potential for a network of sensors - which could in theory beam information wirelessly - to be put together in a short time.

Strano is currently looking at how to develop his SWNT technology to create a practical device. 'My students and I are organising a company that is going to be able to address this issue,' he says. 'The path from taking something that we have done in the lab to something that is handheld is an engineering one, mostly dealing with sample handling and maybe some other innovative concepts too.'

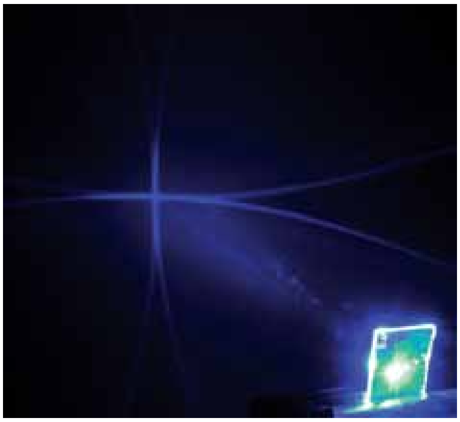
Improving sample collection

For David Atkinson, who heads the Initiative for Explosives Detection at Pacific Northwest National Laboratory (PNNL) in the US, sampling is the biggest issue when it comes to detecting trace chemicals. 'There is an unequal balance of research time and money put into the detector side versus the sampling side, yet the sampling is just as important as the detector,' he says.

In airports, for example, it is now fairly standard practice to test suspicious objects using a wipe that can be heated to release any entrapped particles for analysis using an ion mobility mass spectrometer. However, most molecules in explosives have a very low vapour pressure making them hard to detect using mass spectrometry. Atkinson's team has been researching better materials to use as wipes for this purpose and has developed a functionalised fibreglass. 'We have developed nice, robust materials that have a surface chemistry that has a much higher affinity for explosives,' he says. The new wipes pick up, and release for analysis, far more particles than commercial wipes, he says.

'We can detect single explosive molecules adsorbing onto a single carbon nanotube'

Detecting particles stuck to objects such as shoes or laptops has its drawbacks, not least because a careful terrorist can quite easily



Fluorescent organic dyes can make lasers that dim when exposed to explosive molecules

A whiff of ketones

Matching the versatility and sensitivity of a dog's nose is difficult

When dogs sniff out explosives, it's not the nitroaromatic compounds they are detecting but instead the ketones that are used to purify them. The dog's ability to detect this secondary signature is exemplary, but because ketones are so ubiquitous in nature it is hard to develop technology that is able to pinpoint those linked to explosives.

Tim Swager's team at Massachusetts Institute of Technology is, however, keen to rise to the challenge. They are currently building sensors for the cyclic ketones commonly used in explosives purification, starting with cyclohexanone. This ketone is used to recrystallise RDX (1,3,5-trinitro-1,3,5-triazacyclohexane), a particularly challenging explosive to detect directly, owing to its comparatively low vapour pressure.

The method uses a fluorescent polymer with a fluorophore embedded in it that interacts with a specific ketone. The setup relies on the polymer amplifying the emission from the fluorophore through energy transfer. 'We designed the system to break all the rules of what people thought should happen in energy transfer,' says Swager. Excited electrons transfer between the energy-emitting fluorophore and the absorbing polymer because of orbital overlap. The fluorophore–polymer system acts like an antenna, collecting energy and funnelling it into small sites that are very bright and emit disproportionate amounts of energy, explains Swager. When a target molecule binds to the fluorophore, its shape changes slightly so that the electron transfer can no longer happen, and the light is turned off.

The polymer films have 'exquisite selectivity' for cyclic ketones, say the researchers. In lab tests, the polymer films had a detection limit of less than 5ppm cyclohexanone. Swager is very hopeful that Flir Systems, which sells commercial versions of his original fluorescence detectors, will take on the new device.

FURTHER READING

J R Cox, P Müller and T M Swager, *J. Am. Chem. Soc.*, 2011, **133**, 12910 (DOI: 10.1021/ja202277h)

ensure that everything he carries is free from the loose particles.

Other types of airport detectors suck air through metal meshes that trap any 'sticky' vapourised explosives compounds. The meshes are then heated up and molecules sent through a detector. Atkinson's team has used the same surface functionalisation technique he developed for the wipes to modify some of these metal wires to encourage explosives molecules to stick better.

The PNNL team has also been working on detecting TNT and PETN (pentaerythritol tetranitrate) from chemicals in the vapour phase using mass spectrometry. 'We took a commercial mass spectrometer and did some research on the ion chemistry. We have looked at how we can modify and control the ion chemistry to get the optimal sensitivity and selectivity,' says Atkinson. 'We can now measure 0.09ppt of PETN. We are getting down to a range where we are seeing things at a canine level,' he says.

Two is better than one

'The real strength going forward is combining techniques so you could take a strong trace chemical technique and combine it with, say, a physics-based technique such as x-ray,' predicts Atkinson. St Andrews-based Turnbull is part of a large consortium led by the Royal Military Academy in Brussels, Belgium, to develop tools for humanitarian demining using combinations of very different techniques. The project, which started in January 2012, seeks to combine information from satellite imaging and aerial photography with sensing technology, metal detectors and ground-penetrating radar in a bid to give fewer false positives.

'There are no silver bullets,' says Swager. 'One of the things that held my original technology back was that we couldn't guarantee a 100% solution. It was only when the army in Iraq was getting hit by explosions that people said: "Let's try what we have".' Both he and Atkinson agree that leaps in technology tend to be made after a new terrorist atrocity. 'Something bad has to happen and we do whatever we can to stop it happening again – we accept the imperfect but improved solution,' Swager adds.

One major improvement is the miniaturisation of devices, led by advances in portable consumer gadgets from tablet PCs to mobile phones. 'The components in our devices are getting cheaper, smaller and better,' says Flir Systems' Rose.

She envisages a future where people could carry an explosives sensor on a badge clipped to a shirt pocket or a mini-device that could clip onto a mobile phone.

And what of Swager's arrays of wirelessly linked miniature sensors? 'I think they are going to be necessary some day; that's my fatalistic view,' he says.

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Converting ideas into useful devices has been driven by demand from the military

GETTY IMAGES

Selective wipes and vapour detectors could enhance airport security

Emma Davies is a science writer based in Bishop's Stortford, UK

FURTHER READING

- EPSRC's Hypix project http://hypix.photonics.ac.uk/
- Y Wang *et al*, *AIP Adv.*, 2011, **1**, 032115 (DOI: 10.1063/1.3624456)
- D A Heller *et al*, *Proc. Natl. Acad. Sci. USA*, 2011, **108**, 8544 (DOI: 10.1073/pnas.1005512108)
- F Wang, H Gu and T M Swager, *J. Am. Chem. Soc.*, 2008, **130**, 5392 (DOI: 10.1021/ja710795k)