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INTERROGATION OF OPTICAL pH SENSOR BASED ON SOL-GEL DOPED NEW LUMINESCENT EUROPIUM CHELATE WITH COMPACT PHOTON COUNTING SYSTEM

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Summary
This paper presents recent measurements of novel Eu^{3+}-complex doped sol gel layers (ref 1) which are intended for use as pH indicators, with interrogation by monitoring their fluorescent decay with a compact photon-counting receiver (ref 2). The basic chemistry is outlined and the instrumental arrangement and experimental results are described.

Requirements and basic concept of indicator chemistry
Luminescent lanthanide chelates have many applications, being useful alternatives to standard fluorescent dyes especially when there is significant autofluorescence. They are also useful donors for use in energy transfer experiments to determine static inter-molecular distances. These applications arise because of the chelates' excellent solubility and unusual spectral characteristics, including narrow (< 10 nm) spectral emission, large Stokes shifts (> 150 nm), potentially high quantum yields.
Selvin et al. have synthesized several lanthanide chelates but all show inconvenient excitation maxima around 340 nm. In contrast, our novel long-wave luminescent dye, based on europium luminescence initiated by a covalently-bonded antenna fluorophor, shows excitation maxima at 370 nm where low cost LEDs are now available.
To design sensors of high stability and long lifetime, the sensor matrix and sensor technology are of prime interest. Sol-gel technology enables the production of proton-permeable glassy layers at room temperature and offers simple methods for manipulation of the basic composition, molecular structure, and hence the chemical characteristics of organic matrices.
Time-resolved fluorometry is preferable to conventional fluorometry, since there are no intensity related problems due to turbid samples, self-filter effect, and cuvette geometry. Also, the fluorescence decay time is usually independent of the concentration of the indicator, even when it has been partially modified by leaching out, by decomposition, or by photo bleaching.
In the current work, the Eu^{+3}-complex has been successfully entrapped into tetramethoxysilane (TMOS)-based sol-gel matrices. It was initially found that a Eu^{+3}-complex, which showed useful pH sensitivity in aqueous solution, lost this sensitivity when immobilized in sol-gel matrices. In order to recover this property, the pH indicator bromothymol blue (BTB) was added to the starting sol-gel components and it was found that the useful pH response that was present in water was not only restored, but was actually improved upon.

Instrumentation and experiment for interrogation of Eu^{+3}-complex-doped sol-gel coated layer.
The arrangement shown in fig 1 was used for rapid interrogation of fluorescence lifetime. The arrangement improves signal to noise because the sol-gel coating is illuminated directly with a filtered UV LED source, rather than via an optical fibre probe. This increases illumination intensity by removing optical power loss in the launch optics, illuminates a large coating area, and reduces the background auto-fluorescence signal generated from combined launch and return optics. The main excitation peak occurs at 370 nm, which falls in the absorption band of the pH-sensing layer. It should be noted that this arrangement, which was used to improve signal to noise and reduce self-fluorescence in our measurement, was considered to be only an interim step on the way to developing an all-fibre system for illumination and collection of light. Clearly similar gains in signal can be achieved by using larger input and output fibres or fibre bundles, and self-fluorescence can be reduced by use of separate fibre cables for incident and fluorescent light.

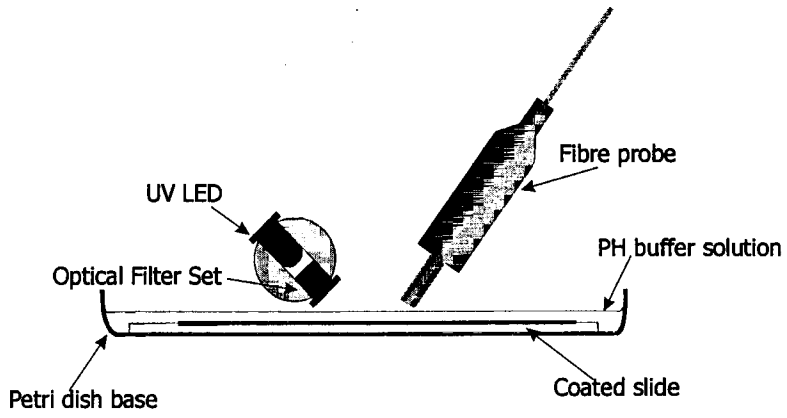

Fig. 1. Optical arrangement for the interrogation of weak fluorescence signals

The fibre probe is then fed back into the interrogation system, where it falls, via suitable long pass optical filtering, onto a compact photon-counting photo-multiplier unit. This is a modified version of that initially reported in reference 2. Custom electronics and specially written computer software allow either real-time measurement of fluorescence lifetime (via the rapid lifetime detection., or RLD, system) or the fluorescence decay to be calculated and displayed as a function of time.

Fluorescence decay profiles from the Eu-complex-impregnated coating (type 'A' made from 2ml TMOS, 2.5 ml EtOH+Eu-complex (2mg) and 1ml HCL 10^{-3}) were examined whilst the coatings were immersed in three pH buffers (pH 4, pH 7, pH 9). The pH of the buffer solutions was verified with a commercial electrode-type pH meter (Jenway 3030) before each experiment.

Fluorescence decay times, taken at the three different pH values, are plotted in fig 2. Two results were taken at a pH of 7. We can see that the fluorescence decay lifetime varies strongly with pH.

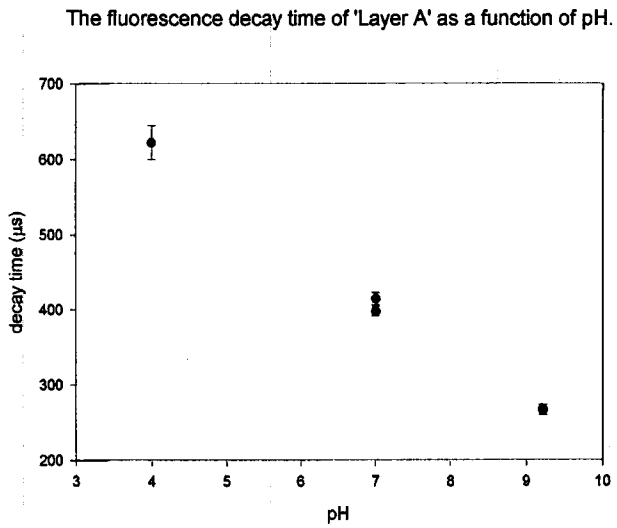

Fig 2. Fluorescent decay times of layer after 15 minutes soaking time

References

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