Time-resolved luminescence of security inks from the UV to NIR

The use of security features, such as luminescent inks, has increased significantly in an attempt to prevent fraud and counterfeiting of materials and goods. Obvious applications of these inks include banknotes, branded goods, drug packaging and food security. Security inks can either show up overtly or be covert, with the latter driving the luminescence further from the visible spectral region into the ultraviolet (UV) and near infrared (NIR) regions. These are regions where light sources are not so common. The use of the luminescence lifetime on top of the wavelength signature adds an extra parameter that can be interrogated.

Overview

As well as being visible to the eye under the correct form of illumination it is increasingly important that security inks can be machine readable. The push towards using more extreme wavelengths for luminescence has been driven by the need for more concealed security features, in addition to overt ones. Hence the need for excitation away from the visible region, towards both the UV and NIR. Security inks also have to be light stable and, in addition to the use of organic dyes, this has led to the incorporation of lanthanides and nanoparticles / quantum dots into flexographic inks. Obvious applications include banknotes and other official stamps. Branded goods and pharmaceuticals also benefit from their use to help monitor for counterfeiting. Another area of security where a more overt colorimetric indicator can be used is food security, where sensing the presence of oxygen is a principal goal – the area of intelligent packaging.

This note aims to show several examples linked to the measurement of different security inks using a range of equipment, with excitation ranging from the UV to NIR. Spatial information is also obtained using time-resolved fluorescence microscopy. The lifetimes recovered span from nanoseconds (ns) to milliseconds (ms).

Time-resolved study of security dye luminescence using UV LED excitation on a *HORIBA Scientific TemPro*

Measurements were made on printed paper, with representative banknote inks, mounted on a front face sample holder using a *SpectraLED-260* for excitation. This long pulse LED emits at 260nm was employed on a *TemPro-01* equipped with a *TBX* detector (see Fig. 1.).

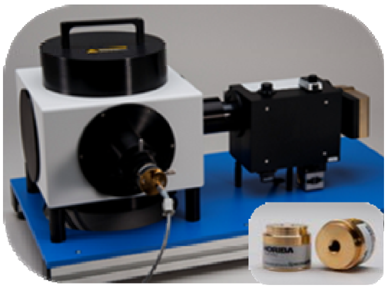


Fig. 1. *TemPro-01* with, inset, *SpectraLED* sources

As well as measuring the time-resolved luminescence decay, having a monochromator enabled the *TemPro* to measure time-resolved emission spectra. After global analysis using *DAS6* software, this allowed the following plot of the decay associated spectra to be made (Fig. 2)

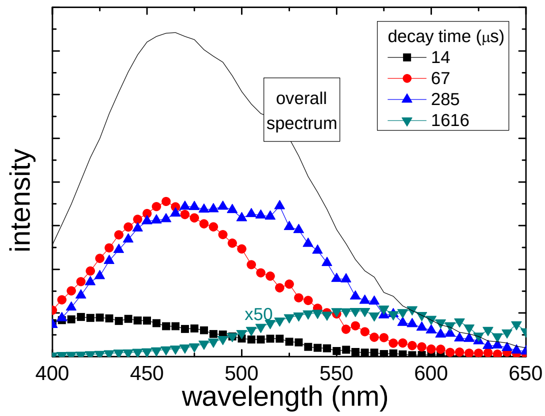
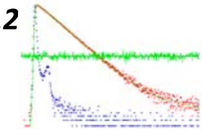


Fig. 2. Decay associated spectra with S-260 excitation

Fig. 2. shows that the decay of the inks on the printed sample is complex, but the *TemPro* measurement allows both spectral and time-resolved information to be obtained in one automated measurement.



FluoroCube NIR measurement of a quantum dot containing flexographic ink

These measurements involved *NanoLED* laser excitation using a wavelength of 980nm and a near infrared detector. In this case the *FluoroCube* was equipped with a MCS card allowing a resolution of 100ns/pt. Note that data with equivalent time resolution can also be acquired using a *TemPro*. The emission of two liquid ink samples containing different quantum dots was measured at both 1115nm (for [**1**]) and 1265nm (for [**2**]). The decays are shown in Fig. 3.

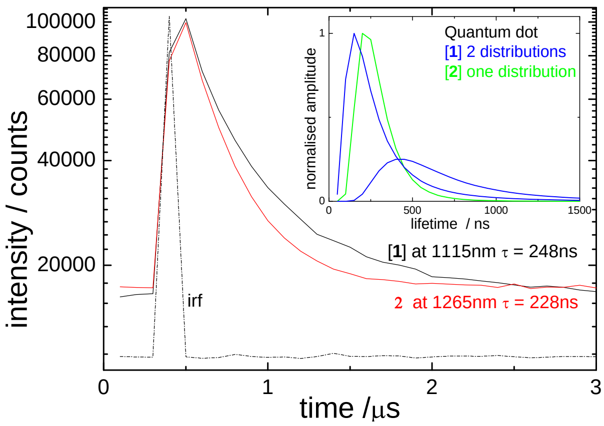


Fig. 3. Luminescence decays for two quantum dot containing ink samples, also showing average lifetimes and instrumental response (irf). Inset distribution analysis for the two samples

The decays were analysed using *DAS6* and found to be multiexponential (3 components in the case of [**1**] and 2 for [**2**]). In another approach, the data was fitted (using *DAS6*) to a distribution function. The outcome is illustrated as an inset in Fig. 3. This shows the potential for the use of these quantum dots, with their added stability over organic dyes in this wavelength region.

Spatial and time-resolved information of ink on a banknote measured using a *DynaMyc*.

At times the ability to obtain spatial information concerning the location of the ink is required. An obvious method to acquire this is the use of time-resolved fluorescence microscopy. An example taken with a DynaMyc is given in Fig. 4. This shows a pattern on a bank note, with a lifetime image superimposed on a camera image. Representative time-resolved decays for two different regions are also shown. The fluorescence decays were analysed as a sum of two exponential decays and the average lifetime calculated.

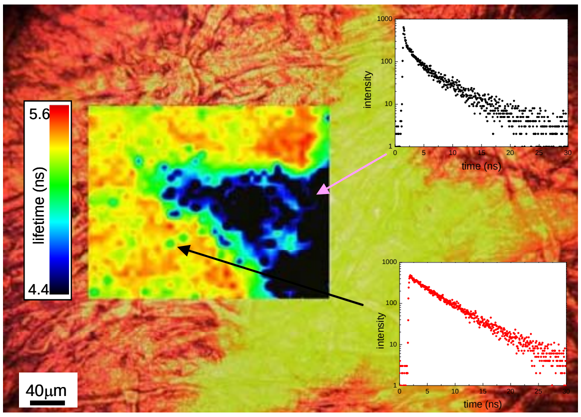


Fig. 4 Fluorescence lifetime image overlaid on a camera image of a patterned area of a banknote. Representative decay profiles are also shown

Summary

This note illustrates how various pieces of instrumentation covering different luminescent time scales and techniques are useful in the characterisation of various security inks, providing value information to help introduce anticounterfeiting measures.