The exceptional near-infrared luminescence properties of cuprorivaite (Egyptian blue)†

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Cuprorivaite (CaCuSi$_4$O$_{10}$, also known as Egyptian blue) exhibits an exceptionally high emission quantum efficiency in the near-infrared region (λ_{max} = 910 nm, Φ_{EM} = 10.5%) and a long excited state lifetime (107 μs); these properties make it appealing for several applications in the fields of biomedical analysis, telecommunications and lasers.

Cuprorivaite (CaCuSi$_4$O$_{10}$) is rare in nature but well known to Egyptologists and museum scientists as the synthetic blue pigment first produced in the 4th Dynasty in Egypt (around 2500 BC) and known as Egyptian blue.[1–4] It was widely used in Egypt and in the Mediterranean basin until the end of the Roman period and beyond.

The first qualitative analyses of the pigment were undertaken by Chaptal[5] and Davy.[6] On the basis of the X-ray diffraction data,[7] the currently accepted chemical formula for Egyptian blue is that of the naturally occurring mineral cuprorivaite. The coloured crystal can be synthesised by heating together, at 850–1000 °C, a calcium compound (typically calcium carbonate), a copper-containing compound (metal filings or malachite: CuCO$_3$·Cu(OH)$_2$), silica sand and soda or plant-derived potash as a flux.[8]

During the past two decades, interest in non-invasive investigations for the characterisation and identification of painting materials has greatly increased.[9] In general, the nature of museum objects is such that sampling is always kept to a minimum and is often completely unacceptable. In this respect, Egyptian blue is an ideal candidate for non-invasive investigations; when excited in the visible spectral window, it shows an intense and broad emission in the near-infrared range.[10] This behaviour has recently been exploited in the investigation and non-invasive characterisation of ancient artefacts, Fig. 1.[11,12]

Here we report a quantitative study of the luminescence properties of CaCuSi$_4$O$_{10}$ in order to determine its quantum efficiency and lifetime. However, the results described here have implications well beyond the field of cultural heritage and may prove to have a variety of uses. For this reason and because Egyptian blue pigment usually contains unreacted raw materials and secondary compounds, such as copper oxides and glass, CaCuSi$_4$O$_{10}$ will be referred to as synthetic cuprorivaite hereafter. Manufactured synthetic cuprorivaite (from Kremer Pigmente) was characterised using X-ray
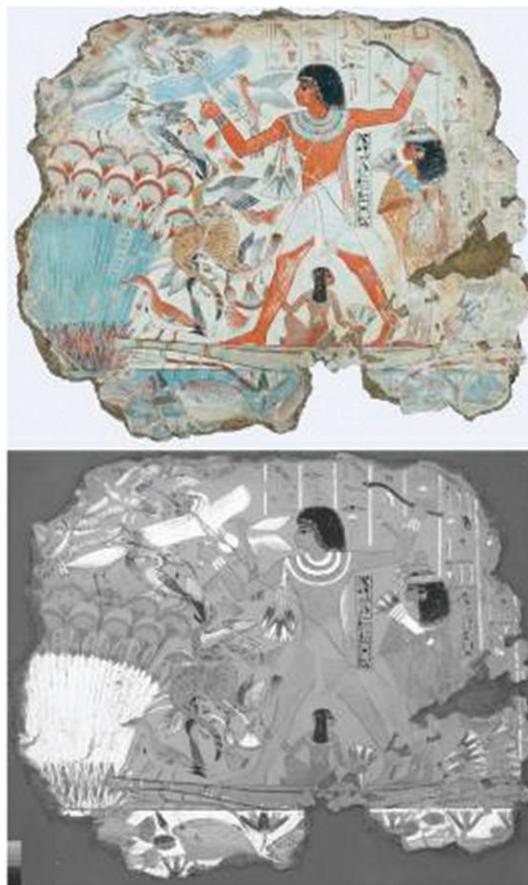

Fig. 1 *Fowling in the marshes* (EA 37977), Nebamun wall painting fragment, British Museum, London, UK: visible (top) and infrared photoluminescence (bottom) images. Bright white areas, which correspond to the presence of Egyptian blue, are caused by luminescence from the pigment. ©*The Trustees of the British Museum*.

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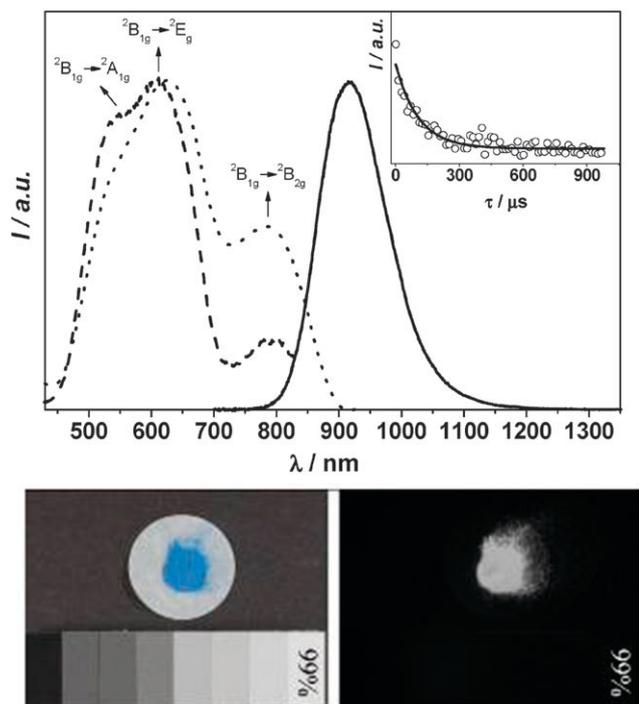
Fig. 2 (Top) Absorbance (dotted line), excitation (dashed line, λ_{em} = 916 nm) and emission (solid line, λ_{exc} = 637 nm, corrected for the detector response) spectra of powdered synthetic cuprorivaite. Inset: luminescence decay (107 μs, λ_{exc} = 637 nm). (Bottom) Visible (left) and visible-induced luminescence (right) digital images (λ_{exc} = 629 nm) of a synthetic cuprorivaite sample captured in the 800–1000 nm range. The 99% reflectance standard is non-luminescent and allows quantification of ambient stray infrared radiation.

diffraction, reflectance and photoluminescence excitation and emission spectroscopy.‡

The compound has been photophysically investigated both as a pure powder and mixed with potassium bromide (around 80% KBr) with identical results. Fig. 2 (top) shows the absorption (total-reflectance) spectrum, the emission (λ_{exc} = 637 nm) spectrum and the luminescence decay profile of synthetic cuprorivaite. Absorption and excitation spectra show three different electronic transitions ($^2B_{1g} \rightarrow ^2B_{2g}$, ^2E_g and $^2A_{1g}$) attributable to Cu^{2+} ions, which are expected to be the only photoluminescent components of cuprorivaite.[10] The emission spectrum is centred at 910 nm and is related to the lowest energy electronic transition ($^2B_{2g} \rightarrow ^2B_{1g}$). This transition is symmetrically prohibited, as suggested by the very long luminescence decay (107 μs; inset Fig. 2). The compound shows an exceptionally high luminescence quantum yield for an infrared emitter, Φ_{EM} = 10.5%. The strong emission can be observed in Fig. 2 (bottom), which shows the visible and visible-induced luminescence images of powdered synthetic cuprorivaite.

The long luminescence lifetime and the unusually intense infrared emission make cuprorivaite an excellent candidate as a luminescent label for a number of applications.

In the bio-medical field,[13] for instance, the greater penetration by infrared photons of human tissue with respect to the penetration of UV or visible photons offers the possibility

of attaining more detailed and highly resolved images.[14–16] Materials that emit between about 700 and 950 nm or around 1050 nm are preferred as this minimizes absorption by the tissue. Thus, excitation between about 650 and 900 nm is required.[17] Moreover, the relatively long-lived luminescence makes it possible to cut off short-lived background emission from biological matrices. This can be easily achieved by setting the instrument to detect the luminescent output after a suitable delay.

Another potential application of this strong NIR emitter is in silica-based optical amplifiers[18–20] and fibre optic systems for telecommunications.[21] For long distance communication it is necessary to compensate for losses in the fibre by regenerating the signal, typically every 50–150 km (depending on the data rate). At present, this is achieved using optical amplifiers, which are typically pumped at 1480 or 980 nm (standard telecommunication window) with commercially available semiconductor diode lasers coupled into the amplifier with a wavelength multiplexer.

NIR emitting species are also useful in laser technology,[22] where the generation of coherent low energy light beams can form the basis of tunable solid-state lasers over a wide spectral range.[23]

Finally, it should be noted that synthetic cuprorivaite is evidently a very stable inorganic material; ancient samples which have survived for millennia in both dry and damp environments still exhibit bright luminescence.[24,25] Similarly, exposure to visible light does not seem to be a problem; objects displayed in museums for several decades have not undergone photo-bleaching (see page 28 of ref. 1).

In conclusion, synthetic cuprorivaite is a stable inorganic compound which exhibits an excited-state lifetime of 107 μs and, to the best of our knowledge, the highest quantum efficiency (10.5%) for a molecule-level chromophore emitting in the 800–1100 nm range. For comparison, currently available near-infrared emitters (mainly lanthanides[26] and d-block metal complexes[27]), commonly used in the applications discussed above, are severely limited by their low emission quantum yield (approximately one order of magnitude lower than that reported here).

The photoluminescence properties of other materials traditionally used as painting materials, such as $BaCuSi_4O_{10}$ (Han blue), $BaCuSi_2O_6$ (Han purple), $BaCu_2Si_2O_7$, $Ba_2CuSi_2O_7$ and $xBaSO_4 \cdot yBaMnO_4$ (manganese blue)—a compound with an emission in the 1140–1160 nm range—are currently being investigated. Ancient Egyptians may not have attained eternal life, but one of their most frequently used pigments may now have a future in a variety of hi-tech applications including bio-medicine, lasers and telecommunications.

Notes and references

‡ X-ray powder diffraction spectra were collected in theta–theta reflection geometry with CuKα radiation on a PANalytical X'PERT PRO diffractometer (PW3050 goniometer equipped with an X'Celerator detector). Reflectance spectra were collected using a

portable spectrophotometer assembled as a prototype from separate components (AvaLight-D(H)-S radiation source and a CCD detector coupled to an integrating sphere by a fibre-optic system). Luminescence measurements were carried out with an Edinburgh FLS920 spectrometer (Xe900 450 W Xenon arc lamp, Hamamatsu R5509-72 supercooled photomultiplier tube at 193 K coupled with a $BaSO_4$ coated integrating sphere). The emission lifetime in the microsecond timescale was measured using a single photon counting system (Edinburgh FLS920 spectrometer, 1 MHz laser diode as excitation source, and B&H GmbH MSA-300 acquisition card coupled with the above-mentioned PMT as detector). To determine the luminescence quantum yield in the NIR spectral window, the method proposed by De Mello *et al.*[28] was followed.

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