Europium in the limelight

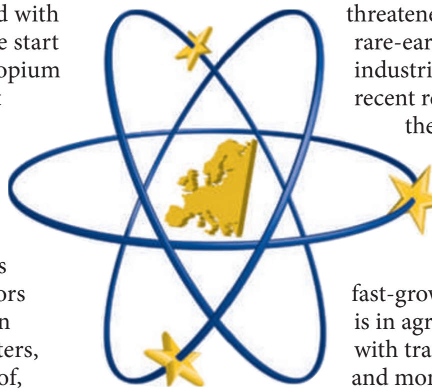
Jean-Claude Bünzli sheds light on why europium — an element that is neither abundant in the Earth's crust nor involved in biological processes — has nevertheless attracted a great deal of interest from chemists.

The story starts at the end of the nineteenth century, when gifted scientists were systematically filling in gaps in Mendeleev's table by deciphering atomic optical spectra. Today this task seems rather easy, and could be carried out by undergraduate students. At the time, however, poorly performing instruments and difficulties in purifying samples were major hindrances. As a result, the history of lanthanide discovery is full of incorrect claims and heated disputes among would-be discoverers.

The first, somewhat furtive, signal from element 63 was recorded in 1885 by Sir William Crookes, who found an anomalous red line (609 nm) in the emission spectrum of a samarium sample. In 1892–3, Paul-Émile LeCoq de Boisbaudran — the discoverer of gallium, samarium and dysprosium — confirmed the existence of this band and detected a further green band (535 nm). Enter Eugène-Anatole Demarçay who, in 1896, after patient fractionation of samarium oxide, determined the presence of a new rare-earth element between samarium and gadolinium. He isolated it in 1901, and ended the note in which he reported this discovery with "I propose for the new element the name europium, with symbol Eu, and atomic weight 151 (approx.)"[1].

The reason why Demarçay decided on this name remains a mystery. Interestingly, he was not affiliated to any university, and had been running an independent laboratory after an unsuccessful application to the Academy of Sciences. He was a rather eclectic scientist who had dealt with organic, organometallic and inorganic chemistry before becoming a talented spectroscopist. He had also toured several countries to study their geology and culture[2]. It is plausible that this opening to all aspects of chemistry and to the world led him to chose Europe over France or Paris (at that time, neither francium nor lutetium were known). Europium metal is now known to be highly reactive; the element's most stable oxidation state is +3, but the +2 state also occurs in solid-state compounds and water.

Georges Urbain, a brilliant young chemist who inherited Demarçay's spectroscopic equipment, observed in 1906 a very bright red emission for yttrium oxide doped with europium[3]. This was the start of a long career for europium as an active component in phosphorescent materials — not only as a red, but also a blue emitter, because its reduced divalent form (Eu^{II}) emits in this spectral range. Phosphors based on red Eu^{III}, green Tb^{III} and blue Eu^{II} emitters, or a combination thereof, can convert UV radiation into visible light. These materials play essential roles worldwide in applications such as X-ray-intensifying screens, cathode-ray tube or plasma-display panels, and have also been used more recently in energy-saving fluorescent lamps and light-emitting diodes.



The luminescence of trivalent europium can also be sensitized by organic aromatic molecules, making such complexes useful in a variety of highly sensitive applications such as security inks and bar codes. For example, when the European Union launched its single currency in 2002, the euro bills were printed with an anticounterfeiting ink at least one component of which is a europium phosphor, most probably a *tris*(β-diketonate), yielding an orange–red emission under UV light. The greenish-blue emission from the same banknotes could well arise from divalent europium but this is mere conjecture.

Since the beginning of the 1980s, europium has played a major role in highly sensitive biomedical analyses that use time-resolved luminescence. Such analyses are routinely carried out in most hospitals and medical laboratories. Luminescent bioprobes based on europium and other lanthanides are now ubiquitous in the life sciences, including bio-imaging. Fortunately, one kilogram of europium is sufficient for almost one billion analyses — which means that these applications are not threatened by the shortage of rare-earth elements feared by industrialized nations after the recent restrictions on exports by the Chinese government.

A recently proposed application that could have far-reaching importance to the fast-growing world population is in agriculture. Plastics doped with traces of divalent europium and monovalent copper have been shown to efficiently convert the UV portion of solar energy into visible light. This process is rather 'green' (the complementary colour of red). Using these plastics to cover greenhouses has enhanced the amount of visible light received by plants, leading to crop yields roughly 10% higher.

Such an increase could cover the growing need for food over several decades without expanding the cultivated surface — showing that europium is possibly heading towards another bright future. ❒

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