MINIREVIEW
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Intriguing aspects of lanthanide luminescence
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The enthralling properties of lanthanide luminescence have propelled luminescent probes, tags and materials based on these elements to the forefront of science and technology. In this minireview, attention is focused on the latest innovations and on less-known aspects of this field. Exciting new developments in bioimaging, therapy, drug delivery, security tags, luminescent sensors, and solar energy conversion are highlighted.

Light and energy for biology and medicine

Luminescence bioimaging features essential attributes such as high resolution and high sensitivity and, depending on the wavelength, high penetration depth. Understanding the structure and functional properties of cells, organs, and living organisms is a key challenge in molecular biology, diagnostics, and therapy. Presently, much interest is focused on two fast emerging areas. The first one is theranostics, which combines the delivery of a therapeutic drug with a diagnostic agent. In this way, the delivery kinetics and treatment efficacy are monitored at the same time with the same biodistribution. Ultimately, there is hope to be able to adapt the therapy and drug dose to specific cases, paving the way for individualised medicine.4 The second aspect is molecular imaging which aims at gaining in vivo target-specific information with high sensitivity; to meet this goal, it seems necessary to design probes mixing different modalities and signal processing.5 In this context, luminescence imaging is of unmatched help. It can be conducted with organic chromophores but their sensitivity to photobleaching, their small Stokes’ shifts and their short excited state lifetimes, which render difficult separation of the probe signal from the autofluorescence background, are often fatal. Since the mid 1980s, lanthanide chelates have successfully supplanted organic chromophores in luminescence immunoassays because they are far less sensitive to photobleaching, lend themselves to time-resolved (TR) detection, and have easily recognisable sharp emission lines; therefore both wavelength and time discrimination concur to isolate the probe signal from the background noise. Lanthanide complexes, polyaminocarboxylates or macrocyclic complexes, are attached onto a specific antibody and luminescence from the emitting ion is detected after the biochemical reaction is completed, either in a two-step procedure or with a one-step, Förster resonant energy transfer (FRET) based protocol. Extension to bioimaging is a logical follow up.
Bioconjugates for sensing, imaging, and therapy

Early imaging experiments with luminescent lanthanide bioprobos (LLBs) conducted in the 1970–1990s did not take advantage of TR detection, most probably in view of the lack of commercial TR microscopes or, rather, of TR microscopes adapted to the slow kinetics of lanthanide luminescence. The first home-made design was described in 1990 for use in immunocytochemistry but even though modification of existing microscopes is rather easy and cheap, the field has been slow to develop despite obvious advantages. Until recently, luminescence microscopy work with LLBs either concentrated on the TR detection of microorganisms in water or presented steady-state or TR images of lanthanide chelates taken up in live cells or tissues. The uptake is usually achieved through an endocytotic mechanism and the localisation within the cell depends on subtle effects and up to now, no obvious relationship with the complex structure has been unravelled. Extensive studies on chelates with cyclen derivatives demonstrated that most complexes localise into the lysosomes while others are taken up by mitochondria, the nucleolus, or the nucleus. On the other hand, all self-assembled complexes studied to date localise in the endoplasmic reticulum, irrespective of the cell type. This leaves little space for selectivity, an unconditional feature in diagnostics and which is largely exploited in immunoassays. Therefore there has been an increasing use of adequate bioconjugates as imaging stains, such as lanthanide complexes linked to proteins, peptides, or antibodies. Important concerns in bioanalysis and bioimaging are the cost of the reactants, particularly of the conjugates, and the analysis time when it comes to fast screening. These problems can be addressed by microfluidics and lab-on-a-chip technologies, as described in Fig. 1 for the simultaneous immunohistochemical detection of two biomarkers expressed by cells in human breast cancer tissue sections. These markers are oestrogen receptors (ER) expressed by the nucleus and human epidermal growth factor receptors (Her2/neu) expressed by the cell membrane. The relative concentrations of the two receptors are relevant for deciding which therapy has to be applied to the patient. For the analysis, 4 μm sections of formalin-fixed breast carcinomas are pressed against the microchannel and the two markers are visualised by a dual indirect immunohistochemical luminescent assay under time-resolved conditions. The initial simplistic microfluidic device allowed the test to be completed in 20 min versus more than 2 h in the hospital and using only 1/5 of the expensive reactants.

Another everlasting quest is the search for more sensitivity, particularly when it comes to detecting cell receptors and/or intracellular analytes. The ultimate dream here is single molecule detection and visualisation of molecule trafficking inside cells; these goals have been achieved during the past decade thanks to improved instrumentation (confocal, epifluorescence, and total internal reflection fluorescence microscopy) and organic or quantum dot stains. An obvious target for lanthanide luminescence is to bring its own advantages to the field. Therefore, lanthanide probes have been encapsulated into nanoparticles (NPs) adequately derivatised; up to a few thousand stains can then be concentrated in one NP and sensitivity is therefore considerably boosted. Advances in the synthesis of NPs allow all kind of sophisticated edifices to be fabricated, based on silica, boehmite, lanthanide phosphate, or single-walled carbon nanotubes. An example of an elaborate probe for single particle detection are nanoparticles obtained from the \[\text{Eu}(_2\text{BHHD})_3(\text{BPT})\] diketonate ternary complex derivatised with (3-isocyanatopropyl)triethoxysilane (IPTES) and further decorated with streptavidin \([\text{BHHD} = 2,6\text{-bis}(1',1',2',2',3',3'\text{-heptalfuoro-4',6'-hexanedion-6'-yl})\text{dibenzohtiophene} \quad \text{and BPT is} \quad 2\text{-}(N,N\text{-diethylaminiin-4-yl})-4,6\text{-bis(pyrazol-1-yl)}-1,3,5\text{-triazine}, \quad \text{see Fig. 2})\]. The 42 nm nanoparticles are strongly luminescent upon visible excitation up to 475 nm and help visualise individual pathogens such as *Cryptosporidium muris or parvum* in water and soft beverages under time-resolved detection. When it comes to cell imaging, small nanoparticles are internalised while larger ones can be used for interacting with markers expressed on the walls of the cells. Another avenue for improving the sensitivity of bioassays is to turn to metal-enhanced luminescence. Encouraging results
have been obtained\textsuperscript{8,25} but this aspect remains largely unexplored and underexploited.

**Multimodal probes**

In addition to theranostic applications which require bi- or multimodal vectors,\textsuperscript{4} there is also much excitement about the possibility of combining two or more imaging techniques in order to remedy the shortcomings inherent to a given imaging technology.\textsuperscript{5,26} For instance magnetic resonance imaging (MRI) displays good spatial resolution but has relatively low sensitivity; adding the high sensitivity of a luminescent probe to a MRI contrast agent is therefore a natural idea. Its realisation is however not very simple since widely different concentrations of the probes are needed. Work is presently being focused on NIR/MRI probes because of the deep penetration of NIR light into biological tissues,\textsuperscript{27,28} at least if excitation can be carried out in this spectral range as well, which still remains to be demonstrated.

**Drug delivery monitoring**

As efforts are presently deployed to deliver drugs where they are needed in diseased organs, there is a need to monitor their delivery and, again, luminescence appears to be the adequate technique. For instance, Eu-doped nanoparticles integrated into the channels of porous silica microspheres (YVO$_4$:Eu$^{	ext{III}}$@SiO$_2$) have low cytotoxicity and owing to large interior space and electrostatic interactions the microspheres have a large loading capacity for doxorubicin (44 wt\%) used in the treatment of a wide range of cancers. Intensity of the Eu$^{	ext{III}}$ luminescence correlates with the cumulative release of the drug at low pH so that the doped and loaded microspheres could potentially be used in gastric cancer therapy.\textsuperscript{29} Several other reports reach similar conclusions.\textsuperscript{30,31} Other types of microstructures designed for delivering a payload along with monitoring or imaging capability include polyelectrolyte capsules obtained by layer-by-layer assembly,\textsuperscript{32} coordination polymers,\textsuperscript{33} or glass nanofibers.\textsuperscript{34}

A new tool in bioanalysis: upconverting nanophosphors

Upconversion is a phenomenon in which two (or more) low-energy photons are absorbed, followed by emission of a more energetic photon. Several mechanisms may be operating and conditions on the involved electronic levels are stringent. In this respect, Ln\textsuperscript{3+} ions with long-life metastable excited states enabling sequential photon absorption are particularly well-suited for generating this type of phenomenon.\textsuperscript{35} The most widely used systems imply two ions: Yb$^{	ext{III}}$ as the sensitizer because it features a relatively intense (by f–f transition standards) absorption around 980 nm and either Er$^{	ext{III}}$ or Tm$^{	ext{III}}$ as the emitter. The first ion has characteristic emissions in the green (530–560 nm) and red (630–680 nm) regions while the second displays upconverted luminescence around 290, 350, 460, 660 and 800 nm.\textsuperscript{36} Doped sodium yttrium tetrafluoride (NaYF$_4$:Yb,Ln, Ln = Er, Tm) is one of the most extensively used materials in bioscience, usually in the form of nanoparticles called upconverting nanophosphors (UCNPs). Although the overall conversion yield remains modest because upconversion is a multiphoton process, UCNPs have made their way in time-resolved immunoassays and are attractive reporters for bio-analytical assays: NIR excitation does not generate luminescence in the analyte and therefore upconverted light can be measured entirely free from any interference.\textsuperscript{37} Technological advances in UCNP synthesis, particularly the core–shell approach, are now at hand which result in emission yields being 1–2 orders of magnitude larger than for the initial materials and reaching several percent.\textsuperscript{18–40} Moreover, plasmonics helps to boost the upconversion yield: UCNPs coated with a 3 nm gold film show ≈ 3-fold luminance enhancement.\textsuperscript{41} All this makes UCNPs easily excitable by LED devices (typically 0.1–1 W power).\textsuperscript{42}

Apart from bioanalysis\textsuperscript{43} and bioimaging\textsuperscript{44} (see next section), UCNPs are operative in NIR light-responsive systems. For instance, when NaYF$_4$:Tm(5%),Yb(30%) core–shell nanoparticles are co-encapsulated into micelles containing a biological payload, irradiation with NIR light releases upconverted UV light, which dissociates the micelles and releases the payload.\textsuperscript{45} The same mechanism operates with hydrogels as well (Fig. 3).\textsuperscript{46} Photocontrolled gene expression\textsuperscript{57} and virus inactivation\textsuperscript{58} have also been demonstrated by using similar methodologies.

UCNPs also function as excitation sources for porphyrin or phthalocyanine photosensitisers (PS) in photodynamic therapy...
of cancer. Instead of irradiating the photosensitisers in the UV-visible range, UCNPs are excited with deep-penetrating NIR light and the upconverted visible light in turn excites the organic photosensitiser, which then produces lethal singlet oxygen (Fig. 4). To this end, UCNPs are coated with a mesoporous silica layer itself doped with the photosensitiser; they are then further derivatised with a monoclonal antibody specific to the bioreceptors expressed by the targeted tumour cells, e.g. MCF-7/AZ bladder cancer cells. Fabrication of the derivatised nanoparticles has to be optimised so that the number of photosensitisers per NP remains large (ideally >1000).

**Small animal imaging**

*In vivo* optical imaging suffers from several intrinsic effects caused by the interaction of light with biological tissues: auto-fluorescence of different endogenous molecules when excitation in the UV-visible range is used, high absorption of haemoglobin in the visible (<600 nm) and water in the NIR (>1000 nm) ranges, scattering. All these factors limit high contrast sensitive optical imaging of deep tissues. So the design of probes which absorb and emit in the biological window is in high demand. Lanthanides can offer several interesting solutions, some of them being highlighted below.

Significant improvements have been achieved by using UCNPs because excitation at 980 nm through Yb\(^{3+}\) and emission either at 630–680 nm (Er\(^{3+}\)) or 800 nm (Tm\(^{3+}\)) lead to interference-free signals and large penetration depths. \(^{48,51}\) *In vivo* demonstration of the effectiveness of the UCNP methodology is now at hand in the case of mice injected with tumour cells pre-labelled with NaYF\(_4\):Yb,Er nanoparticles. \(^{52}\) Fluorescence diffuse optical tomography has demonstrated that hexagonal core–shell UCNPs, NaYF\(_4\):Yb,Tm@NaYF\(_4\) are at least 10\(^4\)-times brighter than two-photon dyes with cross-sections of the order of 100 kGM. In addition enhanced spatial resolution is obtained with UCNPs, as compared to available commercial NIR-emitting two-photon dyes. \(^{53}\)

Heteroepitaxial growth of CaF\(_2\) shells onto α-NaYF\(_4\):Yb,Tm nanoparticles allows one to eliminate surface quenching effects and increase quantum efficiency by 35-times to reach 2% per W cm\(^{-2}\) at tissue-friendly power densities (0.3 W cm\(^{-2}\)). Small-animal whole body imaging using mice intravenously injected with an aqueous dispersion of these UCNPs results in an improved signal-to-background ratio of 310. In addition, model experiments with thick pork tissue show the possibility to obtain images as deep as 3.2 cm. \(^{56}\)

Recent developments of downshifting lanthanide inorganic fluoride nanoparticles have also demonstrated their feasibility to be used as probes for *in vivo* small animal imaging. Thus, ligand-free core–shell NaGdF\(_4\):Nd(3%)@NaGdF\(_4\) nanocrystals excited at 740 nm show efficient emission arising from the \(\text{F}_{4/2}\) level of Nd\(^{3+}\) at 900, 1050 and 1330 nm with a quantum yield of 20%. \(^{49}\) After subcutaneously injecting aqueous dispersions of these NPs at ~3 mm depth into a nude mouse, emission of Nd\(^{3+}\) can be easily detected at 900 nm under excitation in the range 710–760 nm.

Reports dealing with applications of lanthanide complexes with organic ligands for *in vivo* optical imaging remain scarce. The main challenges to be solved here are preventing NIR-emitting lanthanide ions from non-radiative deactivation in order to obtain sufficient emission intensity and shifting of the optimal excitation wavelength towards NIR. Nevertheless, generation-3 polyamidoamine (PAMAM) dendrimer with 1,8-naphthalimide groups grafted at the end of its branches and coordinating eight Eu\(^{3+}\) ions has been demonstrated to target liver in rat hepatic models with good affinity. \(^{57,58}\) This prototype dendrimer can be used to obtain sharp luminescence images suitable for the location of the tumour in the small animal upon excitation at 450 nm and monitoring emission at 610 nm.

Another solution is offered by the use of persistent luminescence nanoparticles (PLNPs). Persistent luminescence is defined as a property of some materials to emit light (during hours or even days) after the removal of the excitation source which might be UV or visible light, electron or plasma beam, X- or γ-rays. \(^{59}\) In such materials, excitation energy is stored in traps followed by its subsequent release by thermal deactivation. Bologna stone gave rise to one of the first observations of this phenomenon, dating back a few hundred years ago. These days the most efficient materials possessing persistent luminescence are Eu\(^{3+}/\text{Ln}^{3+}\) or Eu\(^{3+}/\text{Mn}^{2+}/\text{Ln}^{3+}\) (Ln = Dy, Nd, Tm, Pr) co-doped aluminates, silicates and nitridosilicates. \(^{60}\) As for
other NPs, these nanoparticles can be functionalised and as an example, an assay has been proposed in which z-fetoprotein (AFP) excreted during cancer cell growth can be quantified. The derivatised PLNPs are conjugated to AFP-antibody-coated gold NPs and luminescence can be detected without illumination, which completely eliminates autofluorescence and light scattering. The same advantage stirs interest in PLNPs for in vivo imaging, the principle of which is given in Fig. 5. The reader is redirected to ref. 62 for a comprehensive review of the recent achievements in the field of in vivo applications of PLNPs.

Energizing nanobiodevices with NIR-driven solar cells

A futuristic vision in nanomedicine is to provide nanorobots for in vivo advanced diagnosis, medical therapies, and minimally invasive surgery. These nanorobots integrate embedded nano-electronics and circuitry in order to sense their environment, both mechanically and chemically, for instance for determining local temperature, pH, or concentrations of analytes in blood. As any machine, they of course require an adequate source of electrical energy. Solutions have been proposed for powering these nanomachines in a wireless way: nanogenerators driven by mechanical sources or biochemical nanogenerators such as biofuel cells. Both have their drawbacks so that an alternative way is being explored, taking advantage of the large transparency of biological tissues to NIR light: production of electrical energy from conversion of NIR light by photovoltaic cells.

Initial attempts have been made in 2007 by the group of Chen, who described a device similar to the solar cell sketched in Fig. 6 and into which a 4 μm-thick layer of Na(Y1.3Na0.5)F0.8Yb(20%),Er(2%) upconverting nanorods (0.2 × 1.0 μm) is embedded. When illuminated with a 980 nm laser the nanorods produce an intense upconverted green luminescence and a weaker red one. The porosity of the nanorod layer allows for easy diffusion of the liquid electrolyte so that the resulting incident photo-to-current conversion efficiency is about 80% in the range 480–560 nm. Under 980 nm illumination with 1 W power, the overall laser-to-electricity conversion yield amounts to ηe = 0.047% corresponding to a maximum output power of 470 μW. The yield of upconversion has been estimated to be 0.45%, as compared to about 5% for the bulk material under 200 W cm⁻² illumination, which leaves space for improvement.

Indeed, a better version of the device has now been proposed: (i) hydrophilic nanoporphosphors NaYF₄:Er(2%),Yb(20%) were prepared via one-step hydrothermal synthesis and (ii) biological compatibility has been enhanced by replacing the liquid I₂/I₃⁻ electrolyte with a stable succinonitrile-based gel electrolyte. In this device, 93% of the upconverted light is absorbed by the organic dye. Under irradiation with a 980 nm laser delivering 1 W power, the yield of laser-to-electricity conversion is 0.099%, almost double that of the initial solar cell. With skin-safe 720 mW cm⁻² illumination, the new device exhibits a maximum output power of 44.5 μW, corresponding to ηe = 0.039%; the output power reduces to 22.2 μW (ηe = 0.019%) when the cell is covered with 1 mm layer of chicken skin as a model for biological tissues. Although small, this power is sufficient to energize devices fabricated with nanowires or nanotubes, for which the required power is 10 nW per nano item: the chicken-skin covered photovoltaic cell can therefore theoretically power more than 2000 devices.

Security inks and counterfeiting tags

The amazing versatility of lanthanide luminescence, which can be generated in inorganic materials or complexes with organic ligands upon visible or invisible (UV, NIR) excitation, makes these compounds ideal candidates as active components in security inks, counterfeiting tags, or simple identifying codes. The field is vast and not well-known in academia because applications in security-related matters conduct scientists to patent their findings. There are basically two types of luminescent security tags. The first category relies on down-conversion or downshifting and luminescence is excited by UV light. This is the case in euro bills for instance, which contain Eu⁻³ (orange-red emission) and Eu⁵⁺ (blue and green emission) phosphors (Fig. 7). Mixing different phosphors with different lanthanide ions and concentrations results in millions of potential combinations, an ideal situation for tagging all kind of products, ranging from fabrics to explosives, as well as various batches of the same material.

The second category relies on upconversion and, although other UCNPs can also be used, the ubiquitous β-NaYF₄:Yb,Ln (Ln = Er, Tm) nanoparticles play an important role. Indeed, in the case of Ln = Er, the ratio of the red to green emission, as well as the corresponding lifetimes, can be tuned by varying the composition of the nanocrystals as well as their morphology, not to mention excitation power. This fine tuning allows one
to generate a wealth of potential combinations which can then be used as unique identifying fingerprints. More combinations can be generated by mixing two types of nanoparticles. As an example, inks incorporating nanoparticles doped with either ErIII or TmIII, capped with oleic acid and dissolved in toluene with poly(methyl)methacrylate as a binding agent, are proposed for printing quick response (QR) codes. Very small amounts of ink are needed and the ink is both photostable and mechanically stable.$^{73}$

Luminescent probes and sensors

The fine splitting generated by ligand-field effects on 4f electronic levels is very well understood and the resulting fingerprint nature of optical spectra has been long used for probing the structural environments of LnIII ions embedded in various types of materials and molecules.$^1$ Additionally, excited state lifetimes are reporters of non-radiative deactivation and empirical relationships have been worked out which link non-radiative rate constants with the number of high-energy oscillators in the surroundings of the LnIII ions, leading to hydration number determinations.$^{74}$ Two recent developments in these matters deserved mention.

Probing incommensurate crystals

Most crystals have an ordered 3-dimensional (3D) periodic structure which can be described by conventional crystallographic theory. However, some compounds have an incommensurably modulated structure (quasicrystals) for which the Fourier transform of the modulation function cannot be expressed entirely by rational coefficients; at least one of them is irrational. As a follow up, a superspace group accounting for the symmetry of the structure has to be considered and the structure solved in a (3D + 1) dimension space. Modulated structures are identified by weak satellites in the lower angle section of the X-ray patterns. Typical compounds displaying this peculiarity belong to the scheelite family, $M_{n}(XO_{4})_{m}$, where M is either a single metal or a combination of up to three elements and $X$ = Mo, W, Nb, V, Ta or, possibly, a combination thereof. In particular, in the series of compounds $Na_{x}Eu_{(2-x)3}MoO_{4}$ ($0 \leq x \leq 0.5$), incommensurability is observed for $x \leq 0.25$. $^{75}$ The structures differ by the distributions of the Na$^+$ and EuIII cations and vacancies on the cationic subset characterised by a two-fold symmetry axis (Fig. 8). Much as in the silicate material $K_{x}[Ln_{3}Si_{12}O_{32}]*xH_{2}O$, $^{76}$ EuIII aggregates occur, which appear as

![Fig. 7](Top) Fifty euro bill illuminated at 366 nm and (bottom) emission spectrum of the orange-red luminescence, typical of a EuIII complex (recorded in the authors’ laboratory).

![Fig. 8](Top) Nearest surrounding of a single EuIII dimer in $Na_{x}Eu_{(2-x)3}MoO_{4}$ (Bottom) Portions of the ab projection of the cation subset; dark and light blue colours correspond to EuIII and Na$^+$ atoms, respectively; vacancies appear as large white stars while EuIII dimers are surrounded by yellow contours. Reproduced with permission from ref. 75, © 2012 The Royal Society of Chemistry.

![Fig. 9](Overall (ligand excitation) and intrinsic (f–f excitation) quantum yields, $Q_{Eu}^{L}$ and $Q_{Eu}^{ff}$, and observed lifetimes $\tau_{obs}$ as functions of the relative amount of EuIII dimers with respect to the total amount of EuIII ions, $N_{Eu-cl}/N_{Eu-total}$, in $Na_{x}Eu_{(2-x)3}MoO_{4}$. Reproduced with permission from ref. 75, © 2012 The Royal Society of Chemistry.)
Eu-pairs isolated from all other Eu\textsuperscript{III} atoms by Na\textsuperscript{1} cations and vacancies. These Eu\textsuperscript{III} dimers are responsible for the photophysical properties of the sheelite, which correlate well with the number of such dimers in a given structure. This is demonstrated in Fig. 9 in which reasonable linear relationships are observed for quantum yields and lifetimes versus the relative amount of Eu\textsuperscript{III} dimers.\textsuperscript{75}

**Luminescence quenching by CH/CD vibrations**

Quenching of Ln\textsuperscript{III} luminescence by high energy vibrations (typically X–H oscillators, X = C, N, O) is usually modelled in a simplified way taking into account Förster type transfer and the energy gap law: the fewer phonons needed to bridge the gap between the excited state and the receiving state, the more probable the deactivation. As a straightforward consequence, the replacement of the H atoms by either D or halogen atoms usually leads to large, albeit variable, improvements in emission intensities and is commonly applied to photonic materials, for instance those intended for telecommunications.\textsuperscript{77} Alternatively, the NIR-emitting ions can be inserted into C\textsubscript{4v}-symmetrical supramolecular entities of the form [host\textsubscript{1}-Ln\textsuperscript{III}]\textsubscript{2}\textsubscript{host\textsubscript{2}}, where host\textsubscript{1} and host\textsubscript{2} are 12-metallacrown-4 and 24-metallacrown-8, respectively.\textsuperscript{76} But in any case, understanding the mechanism of nonradiative deactivations is essential for designing luminescent materials, either by (usually) minimising them or increasing them (in some high-power multi-level lasers).\textsuperscript{78} It is however always important to question prevalent scientific assumptions.

During the course of a detailed study of nonradiative deactivation by C–H and C–D vibrations in lanthanide cryptates, Seitz and collaborators\textsuperscript{80,81} have indeed unravelled a counter example: the [Pr(bpy\textsubscript{3})\textsubscript{3}]\textsuperscript{3+} cryptate (bpy is bipyridine) which has been deuterated to various extents (D\textsubscript{n}n = 4, 6, 8, 10, 12, 18, 20, 24, and 30). Global fitting of the nonradiative deactivation rate differences between isotopolog C–H and C–D oscillators revealed that aromatic C–D overtones quench the emission of the 1\textsubscript{D\textsubscript{2}} level more than C–H vibrations. The explanation is given in Fig. 10. The third harmonic of the aromatic C–D vibration is in exact resonance with the 1\textsubscript{D\textsubscript{2}} level, while the second harmonic of the corresponding C–H vibration lies slightly below. That is, the Franck–Condon factor for the latter is smaller, which results in less quenching of the 1\textsubscript{D\textsubscript{2}} luminescence. As a conclusion, if replacement of H by D or Hal atoms is usually beneficial, Franck–Condon factors must be considered with care if the extent of the modification is to be predicted and, in some unfavorable instances, this replacement may lead to larger quenching.

**Pressure and impact sensors (triboluminescence)**

Some crystalline materials emit light when they are crushed, rubbed, or scratched; the phenomenon, triboluminescence, is thought to arise from the recombination of charges produced by the breaking of chemical bonds under mechanical stress and is usually associated with asymmetric crystal structures. Yet, efficient centrosymmetric triboluminescent compounds have been reported.\textsuperscript{83,84} Apparently other origins and mechanisms for triboluminescence exist but they are not yet fully understood. Lanthanides, especially Eu\textsuperscript{III} and Tb\textsuperscript{III} salts and complexes, are prone to this phenomenon and therefore they have been proposed as damage sensors.\textsuperscript{85,86} When it comes to the classes of compounds involved, Ln\textsuperscript{III} β-diketonates are often cited,\textsuperscript{87} e.g., Eu\textsuperscript{III} tetrakis(benzoylacetone) ternary complexes with triethylammonium, Eu\textsubscript{D}4TEA,\textsuperscript{88} or the ~8-times more efficient one with morpholine.\textsuperscript{89} Coordination polymers of Ln\textsuperscript{III} tris(hexafluoroacetyleacetone) with 3,3′-bis(diphenylphosphoryl)-2,2′-bipyridine\textsuperscript{90} or 1,4-dimethylthephthalate\textsuperscript{90} also display this phenomenon.

Until recently, due to the specificity of triboluminescence and the inexistence of commercially available equipment, the efficiency of triboluminescence processes have usually been estimated only qualitatively; compounds with emission visible to the naked eye under daylight are rated as highly triboluminescent and suitable for practical applications. Now, a...
quantitative instrument is at hand in which the drop of a 130 g steel ball triggers the triboluminescence of the sample (Fig. 11); the reproducibility is better than 10% and quantum yields relative to ZnS:MnII have been determined for a series of commercially available phosphors. It is worth mentioning that not only triboluminescence efficiency but also emission persistence have to be taken into account in view of practical applications. For instance, EuD₄TEA is twice as luminescent as ZnS:MnII but its emission disappears more quickly, after 10 drops of the steel ball vs. 50 drops for ZnS:MnII. There is no doubt that such a device will prompt more thoughtful developments of triboluminescent materials and impact sensors now that highly emissive materials are at hand. Indeed, it has been demonstrated that doping the phosphor EuD₄TEA with a carefully adjusted blend of CuII, MgII, FeII, MnII and CuII ions increases its emission intensity by up to 55%.

Helping converting solar energy

Declining fossil fuel reserves and public reluctance to accept nuclear power have urged scientists to find alternative sources of energy. Despite some obvious inconveniences, solar energy is a natural target in view of its availability in large quantities (1000 W m⁻²). Commercial silica-based solar panels routinely have conversion efficiencies between 15 and 20% while multi-junction semiconductor (e.g. InGaP, GaAs, InGaAs) cells reach 37.5% (and over 43% under concentrated illumination). On the other hand, the more convenient dye-sensitized solar cells (DSSCs) experience difficulty in attaining efficiencies >12%. Spectral mismatch between the absorption spectrum of the semiconductor or dye and the solar emission spectrum is a major reason for these relatively low conversion yields. Indeed, semiconductor materials perform best at a wavelength which depends on their bandgap E₉ (in eV; e.g. 1.1 eV ≡ 1.1 μm for Si) according to:

\[ \lambda_{opt} = \frac{1240}{E_g} \text{ [nm]} \]

One solution for enhancing photovoltaic conversion is consequently to fit solar cells with wavelength converting layers (WCL) which absorb in spectral ranges where the photosensitive material does not absorb well and emit in the best-conversion spectral range of the semiconductor. UV/blue light can be converted into visible emission by downconversion, a process in which an energetic photon is “cut” into two longer-wavelength ones, or by downshifting in which one energetic photon is converted into a visible one. Similarly NIR light can be upconverted by absorption of two (or more) low-energy photons and emission of a visible (or UV) one (Fig. 12). Multi-electronic level lanthanide ions are among the best candidates as photoactive cores in wavelength converting materials, particularly in view of their ability to lend themselves to upconversion.

The number of articles reporting lanthanide-based wavelength converting layers for solar cells has been burgeoning during the past few years. A brief summary of the best performing materials is given in Table 1. Assessing the real role of the WCL is however not easy because adding an extra layer to a solar cell modifies its optical properties (reflection, refraction) in either a detrimental or beneficial way. In addition, reports often lack the necessary control experiments. Another point is that many published improvements are for cells with low yields with respect to the practical ones and extrapolation to cells with higher yield is not granted. Nevertheless, examination of dozens of available reports points to the demonstrated following performances for Ln-based WCLs:

![Fig. 12](image.png) AM1.5G solar irradiance spectrum (1000 W m⁻²) along with fractions absorbed by thick silicon wafers (about 58%) and available for downconversion or downshifting (about 16% up to 500 nm) and upconversion (about 16% in the range 1.2–2.5 μm). Redrawn after ref. 97.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Mech.</th>
<th>Material</th>
<th>Δη/%</th>
<th>η/%</th>
<th>Ref.</th>
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</thead>
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<td>9.1</td>
<td>103</td>
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<tr>
<td>mc-Si</td>
<td>DS</td>
<td>[Eu(NO₃)₆(trz1)] as 3-layer LSC</td>
<td>28</td>
<td>19.2</td>
<td>105</td>
</tr>
<tr>
<td>mc-Si</td>
<td>UC</td>
<td>NaYF₄:Er(2%) rear layer</td>
<td>8.6</td>
<td>8.3</td>
<td>106</td>
</tr>
<tr>
<td>DSSC</td>
<td>DS</td>
<td>TiO₂:Eu nanorod layer</td>
<td>13</td>
<td>8.0</td>
<td>107</td>
</tr>
<tr>
<td>DSSC</td>
<td>DS</td>
<td>Gd₂O₃:Eu(6%) in TiO₂ electrode</td>
<td>17</td>
<td>7.0</td>
<td>108</td>
</tr>
<tr>
<td>DSSC</td>
<td>DS</td>
<td>[Eu(C₄)₉(BPBA)] doped into TiO₂</td>
<td>22</td>
<td>9.3</td>
<td>109</td>
</tr>
<tr>
<td>DSSC</td>
<td>UC</td>
<td>Ln₅O₃: 3.3% in TiO₂ electrode (Yb : Tm ratio 10 : 1)</td>
<td>10</td>
<td>7.1</td>
<td>110</td>
</tr>
</tbody>
</table>

* c-Si: crystalline silicon cell; mc-Si: multicrystalline silicon cell; DSSC: dye-sensitized solar cell. DS = downshifting; UC = upconversion. ORMOSIL: organically modified silica glass; LSC: luminescent solar concentrator; chemical formulae are given in Scheme 1. Absolute conversion efficiency of the improved cell.
• Silicon cells: downshifting can add 1–2 absolute% to the conversion yield and upconversion 0.5–1%
• Dye-sensitized cells: +1 to 1.5% for downshifting and +0.2–0.5% for upconversion.

It is anticipated that with the exception of downshifting in dye-sensitized solar cells, these numbers will be doubled in the forthcoming years (particularly if plasmonics are used to dye-sensitized solar cells, these numbers will be doubled in the 0.5% for upconversion.

Conclusions

Although lanthanide luminescence and its applications are now well known and used in many very different fields, much remains to be discovered and improved. One of the major advances in the past decade has been the engineering of highly luminescent and functionalised nanoparticles (including upconverting and long-persistence luminescent nanoparticles). Their ability to form bioconjugates opens vast horizons for bioanalysis, bioimaging, therapy, and drug delivery. We are convinced that this type of applications will be a powerful drive for engineering improved syntheses and for tailoring more elaborate edifices, not to mention a deepening of our understanding of lanthanide spectroscopy. Other fast developing areas include security tags and sensors for which lanthanide luminescence is a real bonanza, as well as photocatalysts. Indeed, if simple enough designs can improve the conversion yield of solar cells by a few percent, lanthanide luminescence will have contributed substantially to a more sustainable world. We hope that the various aspects highlighted in this minireview, although far from being comprehensive, will be an incentive for scientists to join the present research efforts in lanthanide luminescence and to contribute to them with their know-how, enthusiasm, and creativity.

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Notes and references
