LEDS

Metal–organic frameworks protect perovskite

The stabilization of perovskite nanocrystals (PeNCs) by a surrounding metal–organic framework (MOF) results in a simple yet effective way to make extraordinarily bright PeNC-based LEDs, with stable continuous operation of up to tens of hours.

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The development of high-brightness light emitters is key to the realization of next-generation, high-definition displays. The International Telecommunication Unit (ITU), a specialized agency of the United Nations responsible for the technical standards of video broadcasting, recommends a high luminance capability of 1,000 to 10,000 cd m^{-2} (BT.2020 or Rec. 2020) at the final system output for the ultra-high-definition screen market.

Perovskite light-emitting diodes (PeLEDs) are potential candidates for future displays owing to their compatibility with low-cost solution-based fabrication as well as their outstanding colour qualities. PeLEDs deliver maximum luminance levels, at the best, reaching the order of 10^4 cd m^{-2} (refs. [1,2]), in principle meeting the BT.2020 brightness, although with no room for system losses. Perovskite nanocrystals (PeNCs) are excellent emitters owing to their high colour purity, which originates from a spectrally narrow emission with a typical full-width at half-maximum (FWHM) of ~20 nm. Furthermore, the colour of PeNC emission can be conveniently tuned simply by controlling the composition, in particular, their halogen content. The result is that it should be possible to achieve a display with a much wider colour gamut using PeLEDs than traditional organic LEDs, which feature broadband emission spectra due to their vibronic coupling. Remarkably, perovskite nanocrystal LEDs, which operate with very high efficiencies of over 20% (ref. [2]), have also been realized.

However, at present, the operational lifetimes of PeLEDs are commonly limited to minutes to hours even when operated at low brightness levels on the order of 100 cd m^{-2}, an order of magnitude far away from the ITU's minimum in BT.2020. The best measured operating hours so far reach a few hundreds of hours for operation at the low luminance level (about 300 hours at 500 cd m^{-2})[3] and at higher operational brightness the device lifetimes drop exponentially. The main problem is that common PeNCs are intrinsically unstable in the films. PeNCs usually degrade into the bulk phase. Particularly under the influence of the electric field applied across the device during operation, ion migration prevails, which is considered to be the most prominent reason for short lifetimes of PeNCs under active device conditions. Keeping PeNCs stable in an active LED while hitting high luminance levels is therefore a major challenge in reaching BT.2020 compatiblity.

Now, writing in *Nature Photonics*, Tsai et al. report the use of metal–organic frameworks (MOFs) to stabilize PeNCs in emissive thin films[4]. The result is an electrically driven active layer of their LEDs (Fig. 1a) avoiding the problems of ion migration and merging into the bulk phase while delivering an impressive maximum luminance level exceeding 10^5 cd m^{-2}.

The authors obtained emissive methylammonium lead tribromide ($MAPbBr_3$) nanocrystals with dual size distributions of around 8 nm and 13 nm in situ in their mesoporous Pb-MOF matrix, which was pre-constructed as a three-dimensional (3D) networked film on the substrate. The final converted Pe-MOF structure exhibits an optical emission with a FWHM of ~20 nm sustained during and after the operation of their resulting LEDs (Fig. 1b). Such MOF-stabilized $MAPbBr_3$ nanocrystal LEDs reach a luminance level of 120,000 cd m^{-2}, a remarkable level in the spectral range of green. When operated at the initial luminance level of 5,000 cd m^{-2} (in the BT.2020 range), the T_{50} lifetime (operational time for electroluminescence intensity level to halve in value) was measured to be 8.3 operating hours and, at the initial luminance level of 150 cd m^{-2}, it was 40 hours. Following the device operation, the PeNCs were shown to be fully free of ion migration or any degradation (Fig. 1b). This achievement is a major milestone towards producing MOF-stabilized PeNC LEDs for BT.2020-compatible bright displays with prolonged lifetimes in the future.

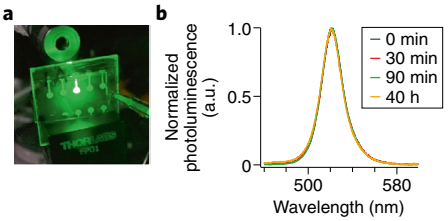

Fig. 1 | MOF PeNC LEDs. a, MOF-stabilized PeNC LEDs under operation. **b**, Photoluminescence spectra of the PeNCs after being electrically driven in the LEDs for hours. The emission spectra are found to be unchanged in terms of both the emission peak and the spectral width. Figure adapted with permission from ref. [4], Springer Nature Ltd.

In the quest for stable PeNCs, ion migration must be prevented to achieve long-term stability as it leads to an unrecoverable decline in device performance. To stabilize PeNCs, various different strategies have been reported, including the use of additives for passivation, doping, ligand engineering and adapting the core–shell architecture of nanocrystals. MOFs have also previously been used as host matrices for PeNCs to improve their stability[5–9]. However, the focus of these earlier studies has not been on electrically driven emissive thin films. The technical challenge here is to deposit a uniform electroluminescent thin film to make quality LEDs while sustaining sufficient electrical conductivity to efficiently inject charge. The critical control parameters are the concentration of precursors and the film thickness to balance the amount of emitter centres forming in the film and the ability to inject charge uniformly into the film. Tsai et al. optimized their Pe-MOF structure to a film thickness of 210 nm.

Making a uniform emissive thin film is critical to fabricating high-performance LEDs. To build a uniform emitting layer, the MOF network will first need to be constructed with good uniformity and coverage. MOFs commonly suffer from poor solubility in

organic solvents, which hinders the formation of a uniform 3D MOF structure across a thin film. To deal with this issue, acid is introduced to tune the pH carefully to dissolve MOF into a clear solution to spin-coat. The Pb-MOF film is then spin-coated to build a 3D mesoporous structure networking Pb with the carboxylic organic bridges. The resulting MOF film is clear and reflective, indicating that the film roughness is reduced. As a next step, the halide salts containing precursors are introduced by spin-coating to convert the Pb-MOF to the Pe-MOF. Using this sequential two-step deposition technique, it has been possible to find an optimal operating window for the Pe-MOF conversion mechanism to yield efficient and uniform emission.

Although the main reason for the short lifetime of PeNCs is considered to be the ion migration triggered under the influence of the electric field applied across the device under operation, there are additional mechanisms that lead to degradation of the device performance, including interfacial or electrochemical reactions, and external factors (moisture and temperature)[10,11]. Although Tsai et al. found that, after being aged by active device operation, their MOF-protected PeNCs were unaffected in terms of their photoluminescence emission peak and FWHM, their LEDs have still demonstrated declined performance, suggesting that there are additional ageing mechanisms. The authors suggested that the device may have been affected by interface polarization. Despite clearly preventing ion migration, the interfaces possibly suffer interface polarization, which suggests that further device engineering is necessary.

The achievement of a maximum brightness above 10^5 cd m^{-2} is an important milestone that was recorded in the current work of Tsai et al. It is remarkable and shows promise for further improved device lifetimes at high brightness. Surely there is a still a long way to push the device lifetimes at the medium-to-high levels of brightness to over 10,000 operating hours. However, it must be noted that organic LEDs reached the required levels of operational lifetimes within 20 years. The impressive progress accomplished by the PeLEDs research community in such a relatively short period of time gives us high hopes for the quest for prolonged stability in the medium-to-high brightness BT.2020-compatible displays in the future. ❐

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Competing interests

The author declares no competing interests.

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PEROVSKITES

Achromatic polarization control in the visible

A special perovskite material design is demonstrated to operate as a wideband, achromatic quarter-wave plate.

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Polarization is one of light's key properties and its control enables the behaviour of light to be manipulated at a fundamental level. It also serves as a valuable degree of freedom that can be harnessed for many applications, ranging from optical interconnects in communications (where waveplates, modulators, and optical isolators are commonly employed) to generating qubits for quantum information technologies (for example, cryptography and computation).

To achieve polarization control, materials must respond differently to different orthogonal states of polarization of light (for example, left versus right circular polarizations or linear polarizations in different planes). This usually manifests itself in the form of dichroism (difference in absorption) and birefringence (difference in refraction). This can be accomplished by selecting specific material structures, or it can be aided via the application of a magnetic or electric field. However, realizing uniform polarization control over a wide wavelength range is often difficult with a single material system, as dichroism and birefringence usually have a strong wavelength dependence.

Now, writing in *Nature Photonics*, researchers in China have demonstrated that a special design of metal halide perovskite crystals can function as a wideband, achromatic waveplate for polarization control[1]. Metal halide perovskites shot to fame in 2009 when it was realized that they could function as highly promising solar cells[2]. In the past decade, the excitement has expanded beyond photovoltaics and they are now actively explored for many other applications, including light sources such as LEDs and lasers[3], X-ray detectors[4] and other tasks. The versatility of perovskites stems from the diverse structures provided by their inorganic framework. While the prototypical 3D perovskite has the ABX_3 formulation (that is, $MAPbI_3$, where MA is methylammonium), quasi-2D, 2D, 1D, and 0D forms exist as well. Combined with a large compositional space, the perovskite structure can be tuned to generate the desired application, such as polarization control.

In general, all perovskite materials can exhibit some degree of circular polarization control in the presence of a magnetic field, as the Zeeman effect induces splitting in degenerate energy levels, based on their