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The key role of the interface in the highly sensitive mechanochromic luminescence properties of hybrid perovskites

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Abstract: Hybrid perovskite (HP) materials are of huge interest in both photovoltaics and lighting applications. Here we report that hybrid perovskite composites, as crystallized powders, can behave as intelligent materials showing highly sensitive and reversible mechanochromic luminescence (MCL). Composites consisting of monolayered 2D HP and 3D HP components exhibit reversible tunable colour emission upon mechanical strain. Spectroscopic investigations first reveal that the bluish-whitish emission of the 2D HP turns into orange in the composite due to an energy transfer process. The bright green emission, observed as soon as the composite is slightly crushed, originates from the 3D HP after efficient energy funnelling from the multi-layered 2D HP produced at the 2D/3D interface by the mechanical treatment. Besides highlighting the key role of the interfaces in light emission of HP, our findings pave the way for hybrid perovskites as highly sensitive MCL smart materials for mechanosensors, security papers or optical storage applications.

Introduction

Halide perovskites may have a 3D (ABX_3 perovskites), or a 2D structure, the latter consisting of layered perovskite networks (corner-sharing octahedra), mainly of Ruddlesden-Popper (RP) type, $(A')_2(A)Pb_nX_{3n+1}$ (<100> series according to Mitzi's description, *n* number of layers).[1] Both 2D and 3D perovskites exhibiting specific electronic and optical properties related to their structural nature, represent a promising class of semi-conductors for photovoltaics[2] or lighting applications.[3,4] Due to high exciton binding energies related to quantum and dielectric confinement effects,[5] layered materials give rise to room temperature narrow emission which can be tuned by means of halide substitutions.[4] When strong exciton–phonon interactions are present, self-trapping of band-edge excitons can give broad band emission attributed to structural distorsions of the 2D perovskite network.[6] In contrast, in 3D perovskites such as $(CH_3NH_3)PbBr_3$ or $FAPbBr_3$ (FA: formamidinium), excitons have low binding energies,[7,8] resulting in low radiative recombination rates. In order to obtain emissive 3D perovskites, a strategy was to spatially confine the charge carriers by making perovskites nanocrystals/quantum dots.[3] A breakthrough was also the incorporation of long chain organic molecules during the synthetic process of 3D systems. On the one hand, such organic entities, particularly of amino-acid type, can have a passivation effect allowing a restriction of crystal grain growth during film formation. As an example, the 5-aminovaleric acid, $^{-}O_2C(CH_2)_4NH_3^{+}$, templates submicrometer-size $FAPbI_3$ platelets, leading to PeLEDs with high external quantum efficiencies (EQE) of 20.7%.[9] On the other hand, such organic entities, as A'^{+} cations, allow the formation of layered perovskites $(A')_2(A)Pb_nX_{3n+1}$ with different *n* values together with the 3D material (known as 2D-3D perovskites). PeLEDs with high EQE are obtained as a result of fast energy funnelling from high band gap domains (small *n*) into low band gap domains (large *n* ≈ 3D component),[10,11] while lower efficiencies are reached with pure layered phases.[12] HP interfaces are extremely important in view of device performances and stability, however, despite the increasing research efforts devoted to the synthesis and characterization of HPs in the last years, a good understanding of the interface chemistry and physics is still necessary to fully exploit the enormous potentiality of HP as functional materials in optoelectronics, photonics, sensors, and other novel technologies.[13]

In this article we present a composite (denoted in the following 2D-C4/3D) consisting of a monolayered <100> type hybrid perovskite $(GABA)_2PbBr_4$ (in the following 2D-C4) ($GABA^{+}$, $HO_2C(CH_2)_3NH_3^{+}$ = 4-ammoniumbutyric acid) and the $(CH_3NH_3)PbBr_3$ (in the following 3D) perovskite, exhibiting remarkable mechanochromic luminescence (MCL) properties and demonstrate the key-role of the 2D-C4/3D interface in the activation of the MCL processes. MCL compounds, mainly AIE organic compounds[14,15] and also metal complexes,[16,17] are materials which change their emission colours when a mechanical force such as grinding is applied, as a consequence of bulk structural or molecular conformational changes. We have recently reported a rare example of HP exhibiting MCL properties with a layered HP belonging to the <110> series.[18] However, in

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that case, as recently reported,[19] the local distorsions induced at the crystal surfaces by mechanical treatments produced only a modest variation in the emissive properties, restored by self-healing, limiting its use as functional material for sensor applications. Here, we show that a pressure applied to the composite with a very slight crushing produces a small amount of multilayered phases (n>1) at the 2D/3D interface, able to activate the bright green emission of the 3D component through an efficient energy transfer. We also show that the close contact between 2D-C4 and 3D components induces a quenching of the 2D-C4 crystal surface emission accompanied with the enhancement of the orange room temperature phosphorescence (RTP) originating from the immobilized GABA$^+$ cations. These results highlight the key role of the interfaces in the light emission processes of halide perovskites and, more importantly, demonstrate the potentialities of HP as intelligent materials in the field of mechanosensors.

Results and Discussion

2D-C4/3D composite: The 2D-C4/3D composite that we define as a mixture of both components $(GABA)_2PbBr_4$ (2D-C4) and $(CH_3NH_3)PbBr_3$ (3D) in close contact can be obtained at room temperature both by a solution process and a solid state process. It must be noted that the synthesis, crystal structure and white light emission of $(GABA)_2PbBr_4$ were recently reported but no emission/excitation spectrum was provided.[20] The solution process consists of a precipitation of an orange powder by addition of ethylacetate into a HBr solution containing the reagents (GABA)Br, $(CH_3NH_3)Br$ and $PbBr_2$ in 2/1/2 ratio (Figure 1a). Solid state ^{13}C NMR[21,22] (Figure 1b) and powder X-ray diffraction (Figure 1c) clearly show that the crystallized powder is a mixture of $(GABA)_2PbBr_4$ and $(CH_3NH_3)PbBr_3$ without trace of potential $(GABA)_2(CH_3NH_3)Pb_2Br_7$ bilayered perovskite whose composition would also correspond to the used stoichiometry. It must be noted that a slow liquid-gas diffusion also leads to crystals of $(GABA)_2PbBr_4$ and $(CH_3NH_3)PbBr_3$ which is in contrast to the synthesis of the iodide bilayered perovskite $(GABA)_2(CH_3NH_3)Pb_2I_7$.[23] This could be related to the lattice mismatch concept:[24] a large difference between structural features associated to the highly distorted perovskite layer in $(GABA)_2PbBr_4$[20] and structural features of $(CH_3NH_3)PbBr_3$ would preclude the formation of multilayered materials. In the solid state process, the powders of both components $(GABA)_2PbBr_4$ and $(CH_3NH_3)PbBr_3$ (1/1 ratio) are placed into a vial which is further shaked during a few tens of seconds. In both cases, the resulting 2D-C4/3D composite exhibits an orange emission under UV light, which is by far different from the emission properties of each component (Figure 1a).

3D $(CH_3NH_3)PbBr_3$ crystallized powders display only a hardly discernible emission at about 568 nm (Table S1 and Figure S1) while 2D $(GABA)_2PbBr_4$ (2D-C4) crystallized powders show a bright (PLQY ≈ 16%) bluish-whitish emission composed by two narrow exciton peaks at 390 and 410 nm with a broad tail extending down to about 600 nm (Figure 2a). The different excitation profiles and lifetimes of the two narrow peaks demonstrate their different origin (Table S1 and Figure S4).

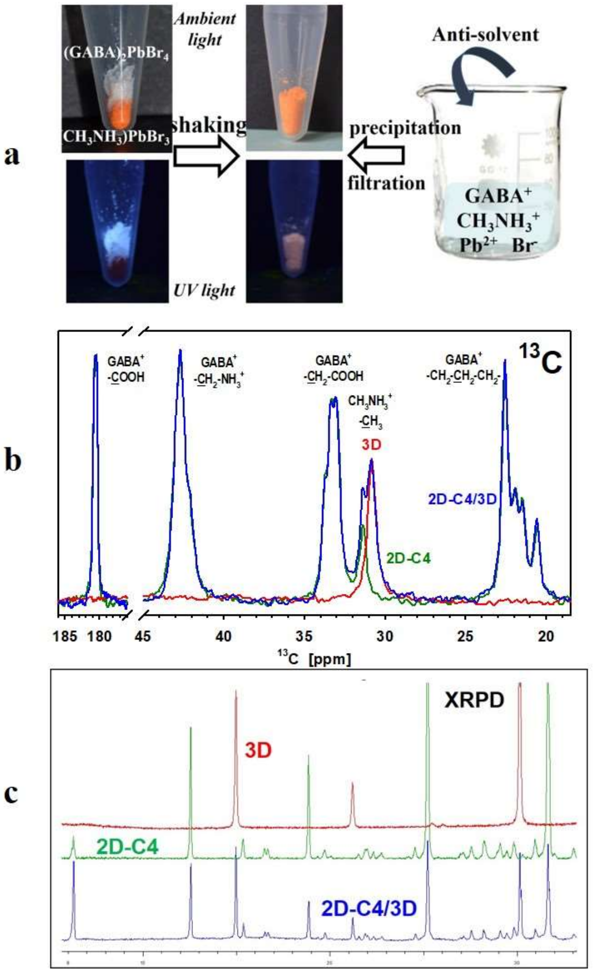

Figure 1. a, Solution (right) and solid state (left) processes giving the 2D-C4/3D composite. Under UV illumination $(GABA)_2PbBr_4$ (2D-C4) displays a bluish-whitish emission while the composite exhibits an orange emission. The same composite can be obtained through the solution process. **b**, ^{13}C solid state NMR (direct excitation) and **c**, XRPD of $(GABA)PbBr_4$ (2D-C4), $(CH_3NH_3)PbBr_3$ (3D) and the C4-2D/3D composite obtained by the solution process.

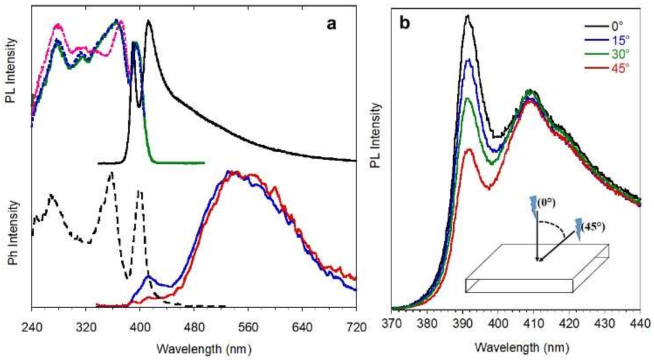

Figure 2. Emission properties of 2D-C4 crystals. **a,** Top**:** Photoluminescence emission (black solid line, λ_{ex} = 290 nm) and excitation (dashed lines: pink, λ_{em} = 392 nm; blue, λ_{em} = 414 nm; green, λ_{em} = 520 nm) spectra; Bottom: phosphorescence emission (blue solid line, delay 0.1 ms, window 1 ms; red solid line, delay 1 ms, window 5 ms; λ_{ex} = 290 nm) and excitation spectra (dashed black line, delay 1 ms, window 5 ms; λ_{em} = 550 nm). **b**, Normalized photoluminescence emission at different incidence angles (λ_{ex} = 310 nm) of a few plate-like crystals lying on the substrate.

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We associate the 390 nm peak to emission from the bulk of the crystals and the 410 nm peak to surface states since its relative emission is enhanced by increasing the incidence angle of the excitation beam (Figure 2b) or by crushing the crystallized powder (see later and Figure S2). Such double exciton has already been observed in layered hybrid perovskites, such as $(C_4H_9NH_3)_2PbBr_4$.[25] However, in contrast to our findings, the low energy and high energy excitonic peaks were assigned to the interior and to the surface/subsurface, respectively, which was tentatively explained by different structural features of the bulk (undistorted perovskite layers) and the surface/subsurface (distorted perovskite layers).[25] According to these observations, the low energy PL peak observed in 2D-C4 would indicate undistorted perovskite layers at the crystal~~s~~ surface while the high energy emission, corresponding to the bulk, is in good accordance with the highly distorted perovskite layers (see ref 19 and Figure S3). Double exciton PL peaks have also been observed for n≥3 multi-layered hybrid perovskites $(C_4H_9NH_3)_2(CH_3NH_3)Pb_nX_{3n+1}$, the lower-energy peak being associated to the emission from "edge states" of perovskite layers/crystals.[26] The two narrow emissions in 2D-C4 display lifetimes in the ns range while the longer wavelength emission tail contains an important contribution with lifetimes in the ms range. By recording the delayed emission spectra we highlight the presence of a broad RTP emission at about 550 nm (Figure 2a, bottom, average lifetime τ_{av} =1.34 ms, Figure S5). Based on our previous findings on 1D hybrid perovskites[27] and on the results reported for mixed-cation perovskites,[28] we assign the RTP to the organic moieties, whose triplet states are stabilized in the perovskite crystal structure (see phosphorescence of the organic (GABA)Br acid salt, Figures S6 and S7). Interestingly, in 2D-C4 crystals the excitation profile of the RTP well corresponds to that of the low energy exciton peak, associated to the crystal surface. These observations support the hypothesis that organic cations located at the crystal surface are responsible of this weak phosphorescence emission.

The emission properties of the 2D-C4/3D composite (QY=8%) (Figure 3) differs from those of its 2D-C4 component in two main aspects: i) the low energy exciton emission is completely quenched; ii) the orange RTP is red-shifted and longer-lived (580nm, τ_{av}= 2.2 ms, Figures S8,S9) displaying, in the steady state spectrum, an intensity comparable to that of the 391 nm exciton peak. We note that such spectral variations can not be ascribed to a trivial re-absorption of the 2D-C4 bluish-whitish emission from the 3D component (Figure S10) since, in such a case, the 391 nm exciton emission would have been quenched as well. We notice that the excitation spectra of the 580 nm broad emission display a sharp peak at 396 nm (red-shifted with respect to the main 391 nm exciton emission) well corresponding to that measured for the low energy exciton peak of the 2D-C4 component (see Figure 2a). We can therefore assume that, in the composite, the low energy exciton emission at 405-410 nm, associated to the 2D-C4 crystal surface, is completely quenched due to energy transfer to the organic component, thus contributing to the observed enhancement of the 580 nm phosphorescence. This phenomenon may be explained by the immobilized and the well-organized self-assembly of GABA⁺ molecules at the 2D/3D interface.

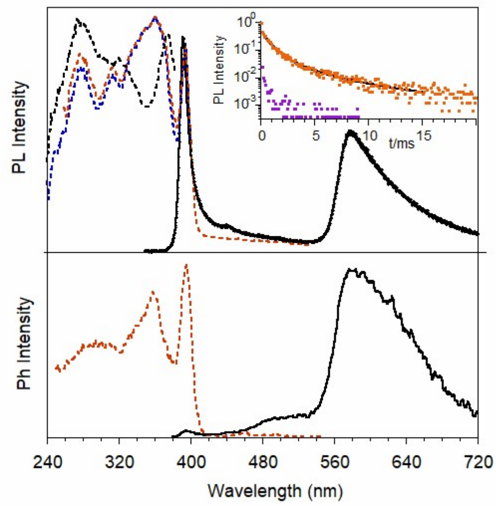

Figure 3. Emission of pristine 2D-C4/3D composite obtained by solution process; Top: PL emission (black solid line, λ_{ex} = 310 nm) and excitation (dotted lines: black, λ_{em} = 390 nm; blue, λ_{em} = 405 nm; orange, λ_{em} = 580 nm) spectra; Bottom: phosphorescence emission (black solid line, delay 0.2 ms, window 2 ms; λ_{ex} = 300 nm) and excitation spectra (dotted orange line, delay 0.2 ms, window 2 ms; λ_{em} = 580 nm); in the inset the time decay of the emission at 580nm (orange dots) and 394nm (pink dots).

Mechanoluminescence: A very slight pressure applied to the composite produces a sharp colour change in the emission, from orange to green (PL QY=7%), clearly observed when the sample is irradiated with UV light. Differently, by applying the same treatment to the separate components of the composite, only negligible changes are observed (see below for a deeper discussion). The sensitivity of the MCL phenomenon is illustrated in Figure 4a: a "spatula" type pen can easily write a "green" message on a sheet once it is dipped into the 2D-C4/3D composite "orange" ink. The quantity of used ink is so small that the message is hardly discernible under ambient light while it appears very bright upon UV illumination (see also Figure S11a and S.I./Video). Very interestingly, the MCL process is fully reversible. By adding some drops of acetone on the crushed crystallized powder, the orange luminescence (UV lamp excitation) is fully recovered after solvent evaporation (Figure 4b). In another way, the pristine emission can be recovered by exposure to acetone vapours.

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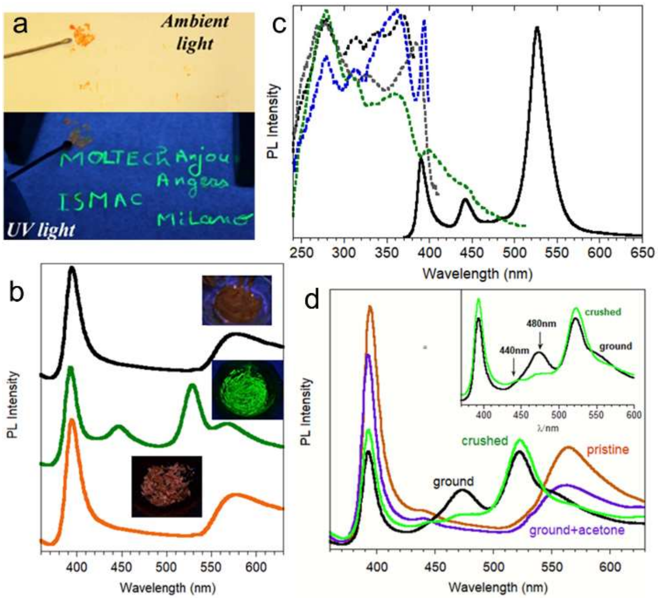

Figure 4. **a,** message written by a “spatula” pen dipped into the pristine 2D-C4/3D composite “orange” ink appears “green“ under UV light (bottom) while it is virtually invisible under ambient illumination (top). **b**, Process reversibility: PL spectra and photos of the pristine (bottom), crushed (middle) and «crushed+acetone» (top) samples. **c**, Emission properties of 2D-C4/3D composite after crushing; PL emission (black solid line, λ_{ex} = 300 nm) and excitation (dotted lines: black, λ_{em} = 390 nm; blue, λ_{em} = 405 nm; grey, λ_{em} = 445 nm; green, λ_{em} = 527 nm) spectra. **d**, Reversible MCL properties of the 2D-C4/3D(x2) composite: the 480 nm band is associated to the formation, upon grinding, of a small quantity of the n=3 RP phase $(GABA)_2(CH_3NH_3)_2Pb_3Br_{10}$.

In order to investigate the origin of the impressive MCL properties of the composite we performed a spectroscopic analysis on its two separate components by applying pressure with a spatula. The nearly non-emissive 3D component of the composite, $(CH_3NH_3)PbBr_3$, displays negligible emission when a weak pressure is applied with a spatula (Figure S11a), while upon strongly grinding for a few minutes, a weak green emission appears (Figure S1, PL QY <0.1%) at about 535-540 nm, even though not visible to naked eye. Green emission is known to be the result of a size reduction of $(CH_3NH_3)PbBr_3$ crystallites that become highly emissive as nanocrystals[3] (for instance the mechanical synthesis of $(CH_3NH_3)PbBr_3$ from $(CH_3NH_3)Br$ and $PbBr_2$ causes the formation of nanodomains of $(CH_3NH_3)PbBr_3$, Figure S11b). However, the different emissive behaviour (intensity and excitation profiles, see Figure S1,S18, Figure 4c) observed by treating the 3D and 2D-C4/3D powders in the same way, demonstrates that the size reduction of 3D crystals in the 2D-C4/3D composite can not be responsible of its impressive MCL behaviour. As regards to 2D-C4, it shows only minor changes in its emission after crushing (Figures S2, S12). The intensity enhancement of the low energy exciton peak at 410 nm, with respect to the 391 nm one, observed after crushing, support the assignment of the 410 nm exciton to crystal surface states.

The spectroscopical analysis of the mechanochromic luminescence properties of the 2D-C4/3D composite obtained by applying pressure with a spatula is shown in Figure 4c. A strong peak at 526 nm appears just after the pressure is applied while the emission at 580 nm is quenched. The emission peak at 441 nm, already apparent in the pristine composite as a very weak shoulder (see Figure 3) is now well evident while a weaker emission at 485 nm appears. The PLE spectra of the different PL contributions are quite different allowing us to speculate on the MCL mechanism. The 526 nm emission can reasonably be assigned to the 3D component of the composite since, by strong grinding the 3D crystals, similar features, although very weak, are observed (Figure S1). Its PLE displays broad bands at 270 and 360 nm (observed also in the 3D crushed crystals) with an additional feature at about 399 nm, similar to the main PLE peak of the 405 nm emission, assigned to the 2D-C4 crystal surface (see Figure 2a). The PLE of the 441 nm emission, peaked at 385 nm, is rather different from the PLE of both the 390 nm and 405 nm emissions, suggesting a different origin. The ^{13}C solid state NMR and X-ray diffraction powder pattern of a strongly ground composite sample do not reveal new phases, but only an amorphization (broader lines) of the 2D component which can be recrystallized upon acetone treatment (Figure S13). An emission around 450 nm has been reported for bilayered (n= 2) $(A')_2(A)Pb_2Br_7$ compounds.[29,30] Even if XRPD does not show such a phase in the 2D-C4/3D composite, a small quantity of this phase, not detectable by diffraction or NMR, could produce the 441 nm emission. In order to better understand this point we prepared through a solution process a composite consisting of 2 $(CH_3NH_3)PbBr_3$ for 1 $(GABA)_2PbBr_4$ (denoted 2D-C4/3D(x2)) from $PbBr_2$, $(CH_3NH_3)Br$ and (GABA)Br reagents in 3/2/2 ratio because this stoichiometry also fitted to the hypothetical n= 3 RP phase, $(GABA)_2(CH_3NH_3)_2Pb_3Br_{10}$. The 2D-C4/3D(x2) composite also exhibits highly sensitive MCL properties, from orange to green emission before and after crushing, respectively. However, besides the 525 nm main emission and the 440 nm band, another band at 480 nm appears after a slight crushing. In addition, a stronger grinding involves the enhancement of the 480 nm band intensity while the 440 nm band disappears (Figure 4d). Such an emission in the 480-500 nm range has already been observed for the n=3 layered perovskites $(BA)_2(CH_3NH_3)_2Pb_3Br_{10-x}Cl_x$ (x= 0, 2).[31] Thus, the 480 nm and 440 nm emissions observed in our systems can reasonably be assigned to a small quantity of $(GABA)_2(CH_3NH_3)_2Pb_3Br_{10}$ and $(GABA)_2(CH_3NH_3)Pb_2Br_7$ multi-layered perovskites at the interface of both components. As shown in Figure 3e and Figure S14 (several cycles), the MCL process of the 2D-C4/3D(x2) composite is reversible. Moreover, these observations have been found to be reproducible for different composite samples, obtained either by solution or by solid state processes (Table S1 and Figures S15-18). As the green emission of the 3D component is correlated to the presence of multi-layered perovskites which contain both $GABA^+$ and $(CH_3NH_3)^+$ organic cations, the use of the (GABA)Br salt, instead of the 2D-C4 perovskite component, could possibly lead to the same phenomenon. We therefore studied the MCL properties of the (GABA)Br/3D composite prepared through a solid state process. Indeed, the non-emissive (GABA)Br/3D composite exhibits a green emission upon grinding. However, we notice that 1) a stronger grinding than for the 2D-C4 composite was necessary to observe the emission, and 2) a spontaneous recovery of the non-emissive pristine composite is observed in air a few minutes after the end of the mechanical treatment, in contrast with the behaviour of the ground 2D-C4/3D composite (Figure S19). This result confirms that the formation of a small amount of multi-layered perovskites activates the emission of the 3D component and demonstrates that only with the two perovskite components 2D (n=1) and 3D highly sensitive MCL properties with controlled reversibility are achieved.

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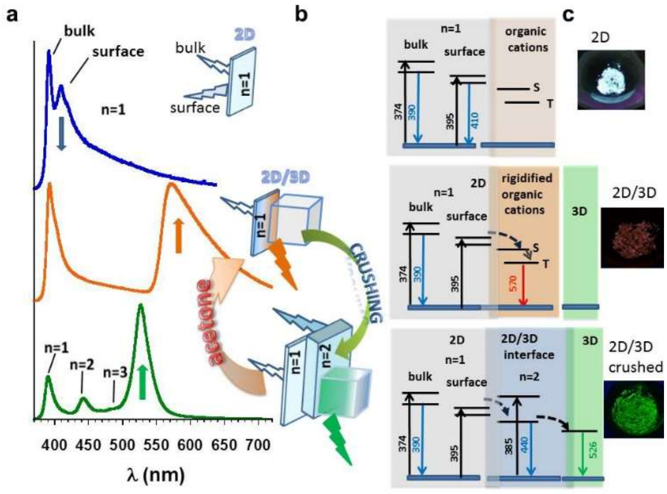

Figure 5. Summary of the photoluminescence processes in the 2D (top), 2D/3D pristine (middle) and 2D/3D crushed (bottom) crystal powders. **a,** Emission spectra; **b**, scheme summarizing the MCL properties of the 2D-C4/3D composite, highligting the key role of the interface between both components; **c**, scheme of the main energy levels involved in the emission processes with photo of the powders under UV illumination.

Figure 5 summarizes the reversible MCL properties of the 2D-C4/3D composite highlighting the key role of the interfaces in emission processes. When the 2D-C4 component, exhibiting bluish-whitish emission (with two exciton peaks 390 nm from the bulk and 410 nm from the surface), is mixed to the $(CH_3NH_3)PbBr_3$ 3D component, its surface exciton peak is quenched partly due to an efficient energy transfer to the organic GABA$^+$ moieties producing a broad orange RTP emission. The impressive MCL observed in the composite is originated by the activation (funnelling effect) of the 3D green emission through n=2 (or n=3) RP phase(s) (Figure S20). In fact, crushing the composite not only gets closer crystallites of both components, but also involves the formation of a small quantity of n=2 or n=3 (2D-C4/3D(x2) composite) RP phases at the interface as highlighted by the observed PL peak around 440 nm (n=2 HP) and around 480 nm (n= 3 HP). The formation of such multi-layered perovskites correlated to the activation of the green emission of the 3D component is in good accordance with previously reported efficient funnelling for mixtures of perovskite compounds as thin film materials, from a n= 2 phase to the 3D one, while in contrast funnelling from a n= 1 phase to n≥ 2 phases is ineffective.[32] An important point is the reversibility of the process. While the crushed sample and associated green emission are stable in air for (at least) a few weeks, the pristine composite (and associated orange emission) can be recovered simply by adding few drops of acetone or by exposure to acetone vapors.

Conclusion

The key role of the interfaces in the light emission processes of halide perovskites has been highlighted by evidencing two distinct phenomena. The first one is the quenching of the exciton emission from the 2D-C4 crystal surfaces accompanied by the enhancement of the organic cations phosphorescence in the 2D-C4/3D composite. The second one is the impressive mechanoluminescence observed in the 2D-C4/3D composite. Upon mechanical treatment a multi-layered structure is produced at the 2D/3D interface able to activate bright green emission from the (otherwise non-emissive) 3D component by energy transfer processes. Our findings pave the way for using powder samples of hybrid perovskites as highly sensitive MCL materials with potentialities of tuning emission colours depending of the nature of organic cations, metal ions or halide, for applications in the field of mechanosensors, security papers or optical storage.

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Keywords: • hybrid perovskite • interface • luminescence • mechanochromic luminescence • perovskite phases

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The key role of the interface in the highly sensitive mechanochromic luminescence properties of hybrid perovskites

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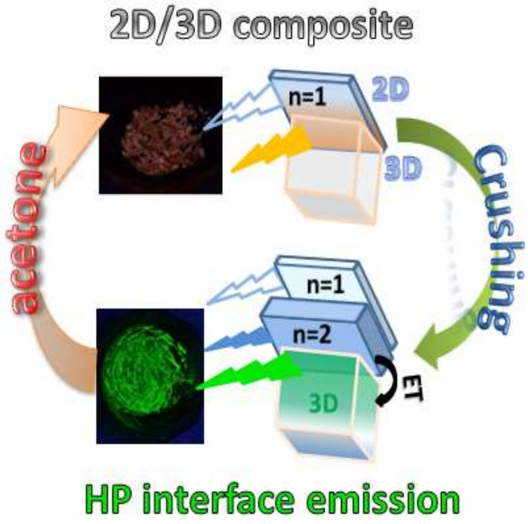

As crystallized powders, hybrid perovskites (HP) behave as intelligent materials showing highly sensitive mechanochromic luminescence properties. Composites consisting of monolayered 2D and 3D HP components exhibit reversible tunable colour emission upon mechanical strain: bright green emission originates from the 3D HP after efficient energy funnelling from the multi-layered 2D HP produced at the 2D/3D interface by the mechanical treatment.

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