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ARTICLE

Colloidal Nano-MOFs Nucleate and Stabilize Ultra-Small Quantum Dots of Lead Bromide Perovskites

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The development of synthetic routes to access stable, ultra-small (i.e. < 5 nm) lead halide perovskite (LHP) quantum dots (QDs) is of fundamental and technological interest. The considerable challenges include the high solubility of the ionic LHPs in polar solvents and aggregation to form larger particles. Here, we demonstrate a simple and effective host-guest strategy for preparing ultra-small lead bromide perovskite QDs through the use of nano-sized MOFs that function as nucleating and host sites. Cr₃O(OH)(H₂O)₂(terephthalate)₃ (Cr-MIL-101), made of large mesopore-sized pseudo-spherical cages, allows fast and efficient diffusion of perovskite precursors within its pores, and promotes the formation of stable, ~3 nm-wide lead bromide perovskite QDs. CsPbBr₃, MAPbBr₃ (MA⁺ = methylammonium), and (FA)PbBr₃ (FA⁺ = formamidinium) QDs exhibit significantly blue-shifted emission maxima at 440 nm, 446 nm, and 450 nm, respectively, as expected for strongly confined perovskite QDs. Optical characterization and composite modelling confirm that the APbBr₃ (A = Cs, MA, FA) QDs owe their stability within the MIL-101 nanocrystals to both short- and long-range interfacial interactions with the MOF pore walls.

Introduction

The main text of the article should appear here with headings as appropriate. Stable lead halide perovskite (LHP) nanocrystals (NCs), with the composition APbX₃ (A = Cs⁺, formamidinium FA⁺, methylammonium MA⁺; X = I⁻, Br⁻, Cl⁻)^{1,2,3,4} have emerged as superior materials for optoelectronic applications such as light emitting devices,^{5,6,7,8} lasers,^{9,10} or selective optical sensors.¹¹ Aided by their intrinsic or surface defect-tolerant electronic structure, LHPs exhibit excellent optical properties that are tunable over the entire visible spectrum through modification of the halide composition. Thus far, the overwhelming majority of studies have focused on the weak confinement regime (i.e. NCs larger than 8 nm) because large NCs are easier to synthesize and stabilize. Nevertheless, smaller NCs are expected to show optical properties that diverge from their larger congeners. For

instance, energy transfer between LHP and external acceptors (e.g. polycyclic aromatic hydrocarbons) only occurs for smaller (5–8 nm) NCs but not for weakly confined donors.¹² However, synthesizing and stabilizing ultra-small LHP NCs (i.e. diameters below 4 nm) is extremely challenging owing to their highly ionic nature, labile surfaces, and metastable structures. Indeed, colloidal syntheses (such as hot injection method) are inefficient for the production of ultra-small NCs due to the fast reactivity of the precursors, which yields nanostructures such as nanoplatelets, nanosheets and nanocubes that are difficult to separate and isolate for further investigation.¹³ Templating agents such as porous silica,¹⁴ zeolites,^{15,16} and metal-organic frameworks (MOFs)^{7,15,17,18,19,20} have been more successful, but so far have also only produced large APbBr₃ NCs with bulk-like emission maxima centered at 520 – 530 nm.²¹ Here, we demonstrate that Cr-MIL-101, a MOF exhibiting large mesoporous cages, is an effective platform for the synthesis and stabilization of highly monodisperse, ultra-small, 3 nm-wide LHP QDs when the MOF itself is in nanoparticle form.

Results and discussions

Owing to their porosity and tunable composition, MOFs have attracted considerable interest for the development of heterostructures where the ordered porosity of the MOF, as host, can be combined with additional electrical, optical, or catalytic properties given by a guest nanoparticle.^{22,23,24,25} There are two well-established routes to immobilize nanoscale objects

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within MOFs: “ship in a bottle” and “bottle around the ship”. Whereas the latter is essentially an encapsulation process whereby pre-formed NCs are added to a solution containing the MOF precursors, the “ship in a bottle”^{26,27} strategy requires that the precursors for NCs penetrate the windows of the pre-synthesized MOFs and react within the pores to form the

desired nanostructure. Ideally, this latter strategy uses the framework skeleton as a ligand shell to lower the surface energy of the nanoparticles and leads to the formation of highly monodisperse NCs whose size is defined by the pore of the MOF host.

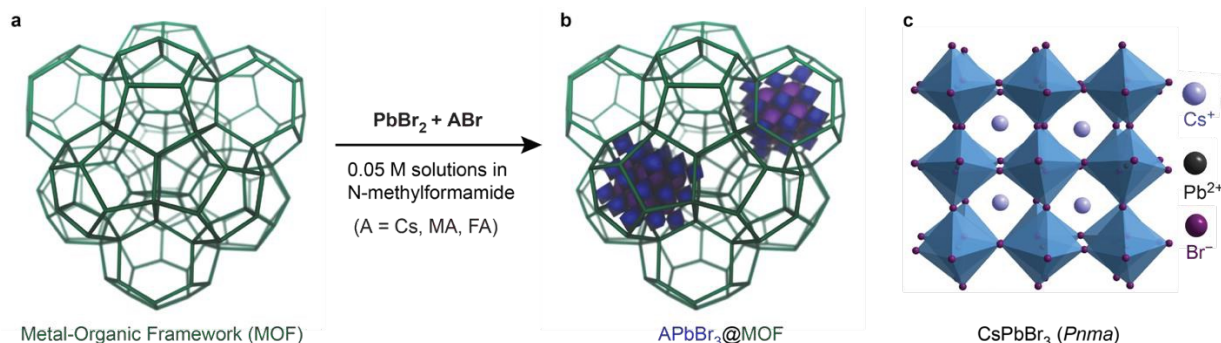


Figure 1. (a) A cartoon representing the 3D porosity of the MOFs before encapsulation of the LHP QDs and, (b) after, where the inclusions represent the LHP QDs trapped inside the pores, (c) crystal structure for γ -orthorhombic CsPbBr_3 ($Pnma$).

APbBr₃ in bulk Cr-MIL-101. Cr-MIL-101 was chosen as a host for the synthesis of halide perovskite QDs because of its large, pseudo-spherical cages, enhanced chemical stability under challenging environments, and relatively well-developed encapsulation chemistry.^{28,29} It can be isolated as a green powder with micron-sized crystals upon reaction of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with terephthalic acid (TA) for 8 hours at 220 °C in acidic media (see Supporting Information for full experimental details). After activation and drying, Cr-MIL-101 retains a zeolite-type MTN framework (a zeolite whose topology comprises two different kinds of subcages: a dodecahedral cage face-shared with four other adjacent cages, Figure 1a) with large pseudo-spherical pores (2.9 nm-wide M cages and 3.4 nm-wide L cages) connected via 1.2 nm and 1.6 nm openings that we reasoned would allow for facile diffusion of LHP precursors into the cages. We found, however, that impregnating micron-sized crystals of Cr-MIL-101 with a

solution of CsBr and PbBr_2 in *N*-methylformamide (NMF) produced mostly bulk halide perovskites attached to the exterior surface of the MOF crystals, regardless of the reaction temperature. Fluorescence spectroscopy of these MOF/LHP composites revealed features dominated by bulk-like emission at 520 nm, suggestive of CsPbBr_3 particles at least 10 nm in diameter (Figure S1). The same spectra nevertheless revealed a small contribution from confined emission at 440 nm, itself suggestive of small nanoparticles possibly formed within the MOF pores. Altogether, the emission data suggested that although the LHP precursors are able to penetrate within the MOF pores, a large concentration gradient is likely established within the relatively large MIL-101 crystals. Rapid nucleation of the perovskite causes blockage of the pore entrance with concomitant formation of predominantly bulk LHP at the exterior and only a small fraction of the desired pore-confined NCs, themselves likely localized near the MOF surface.



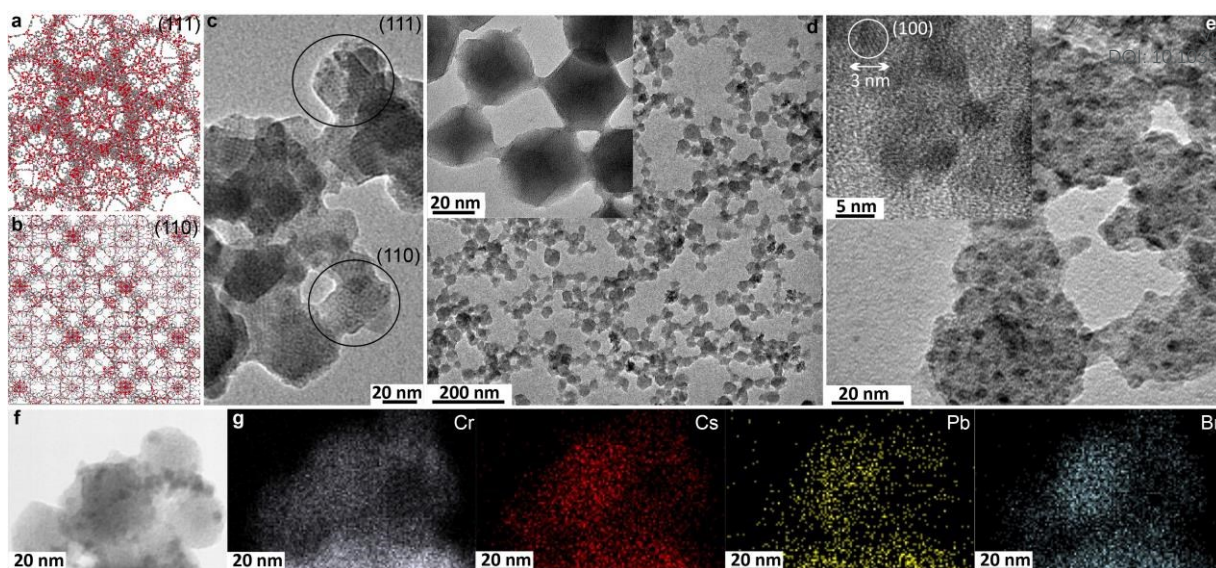


Figure 2. (a) View of the (111) plane in Cr-MIL-101, (b) view of the (110) plane in Cr-MIL-101, (c, d) TEM images for nano-Cr-MIL-101 (approx. 25 nm NPs), (e) TEM images for CsPbBr₃@nano-Cr-MIL-101 (approx. 25 nm NPs), (f) EDX mapping for CsPbBr₃@nano-Cr-MIL-101.

Synthesis of colloidal nano-Cr-MIL-101. Encouraged by the appearance of confined emission in bulk Cr-MIL-101, we sought to improve penetration and achieve even distribution of the LHP precursors throughout the host crystals by employing colloidal MOF nanoparticles. The synthesis of colloidal MOFs has been reviewed recently,³⁰ and includes diverse strategies such as reverse addition of a co-solvent into the reaction mixture, microemulsion methodology,³¹ use of microwaves³² or ultrasound,³³ and addition of a modulator such as a polymer or surfactant.³⁴ Using a modified procedure described by the Edler group,³⁴ we explored various modulators to synthesize colloidally stable, porous Cr-MIL-101 nanoparticles. The fundamental concept is to employ modulators that compete with the direct reaction between TA and Cr³⁺, the two main ingredients for Cr-MIL-101: amines that form acid-base adducts with TA, and monocarboxylic acids that bind Cr³⁺ and ideally provide colloidal stability to eventual MOF nanoparticles. A series of tests showed that benzoic, acetic, an hexanoic acids are ineffective as modulators for the production of colloidal Cr-MIL-101, all yielding either larger crystals or samples with poor crystallinity. Similarly, using hexadecylamine or oleylamine as modulators produced only larger, highly polydisperse NPs with diameters exceeding 50 nm and low colloidal stability (Table S1). However, addition of oleic acid (OA) to the MOF synthesis solution, in a molar OA:TA ratio of 1:12, produced colloidally stable 25 nm-wide Cr-MIL-101 particles with good crystallinity (nano-Cr-MIL-101, Figure S2). After the washing procedure, FTIR spectra (Figure S3) showed complete removal of the modulator since the band associated to free -COOH (from oleic acid) at 1700 cm⁻¹ is no longer present. The vibrational spectrum of nano-Cr-MIL-101 differs from Cr-MIL-101 only due to the presence of NMF (ν_{C-N} at 1310 cm⁻¹), with the NPs remaining colloidally suspended in the solvent of choice (acetone, NMF). The colloidal suspension is stable for over a year in acetone and

NMF without presenting sedimentation while centrifuging the suspension at 4k rpm.

APbX₃ in nano-Cr-MIL-101. Solutions of ABr (A = Cs, MA, FA) and of PbBr₂ in NMF were mixed with a stable, colloidal suspension of monodisperse nano-Cr-MIL-101 in NMF. After stirring these mixtures for 1 to 12 h at room temperature, the reaction mixture remained colloidal, a first sign that bulk LHP did not precipitate under these conditions. Reaction mixtures were subsequently drop- or spin-casted on quartz and glass substrates and dried by heating at 70 °C for 1 min multiple times to produce films with varying thickness between 100 to 300 nm (Figures S4, S5). Optimized reactant ratios, 2:1 CsBr:PbBr₂ for CsPbBr₃ and 1:1 ABr:PbBr₂ for FAPbBr₃ and MAPbBr₃ (Figures S6, S7) produced films where the pXRD diffraction peaks pertaining to the nano-Cr-MIL-101 are broader, as expected for small NCs (Figure S8) but the crystallinity of the nano-MOF host is unaffected (Figure 2). TEM of the nano-MOF-encapsulated LHP nanocrystals revealed consistent sizes of approximately 3 nm, in line with the 2.9 nm and 3.4 nm cage sizes of the MOF (Figure S9). Furthermore, quantitative EDX mapping of the LHP NCs confirmed the ratio of 1:1:2.9 for CsPbBr₃ (Figure 2f,g). As the 3 nm CsPbBr₃ QDs have diffraction features that are too broad to be observed by pXRD (Figure S8), we confirmed their identity by Raman spectroscopy. The latter revealed the [PbBr₆]⁴⁻ vibration³⁵ at 53 cm⁻¹ along with unmodified bands from the MOF host (Figures 3, S10).³⁶ The vibrational band associated with the rattling of the Cs⁺ cation is weak in the bulk and undetectable for CsPbBr₃@nano-Cr-MIL-101. We assign the 20 cm⁻¹ shift of the [PbBr₆]⁴⁻ band relative to bulk³⁷ to a larger contribution from the extended bonds of surface species, which in 3 nm particles represent a much larger proportion of all [PbBr₆]⁴⁻ species than in bulk CsPbBr₃.



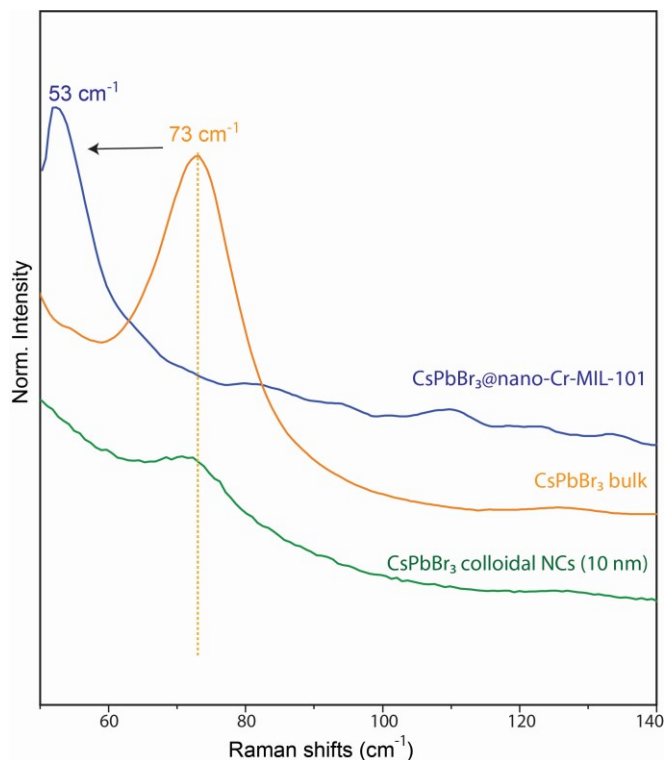


Figure 3. Comparison between Raman vibrational bands of bulk CsPbBr_3 , CsPbBr_3 @nano-Cr-MIL-101, and colloidal CsPbBr_3 NCs (10 nm).

Even when compared to a standard 10 nm colloidal suspension of CsPbBr_3 NCs (79 cm^{-1}),³⁸ synthesized via hot injection method,¹ the observed shift is an indication of the expansion of

bond lengths³⁵ in 3 nm CsPbBr_3 @nano-Cr-MIL-101 (Figures S9, S10). As expected upon partial pore filling, N_2 adsorption isotherms of CsPbBr_3 @nano-Cr-MIL-101 gave an apparent BET surface area of $1257 \text{ m}^2/\text{g}$, a 20–25% decrease (on average, depending on sample) relative to bulk Cr-MIL-101 (Figure S11). Optical characterization provided important information on the nature of the LHP QDs within nano-Cr-MIL-101. Bare nano-Cr-MIL-101 shows two distinct features in the absorption spectrum: one at 447 nm attributed to π - π^* transitions within the phenyl ring of the organic ligand, and one at 599 nm corresponding to the ${}^4\text{A}_{2g}$ - ${}^4\text{T}_{2g}$ transition in Cr^{3+} (Figure 4a). Importantly, the MOF itself is not photoluminescent (Figure 4b). The representative features of the host persist in the absorption spectra after crystallization of APbBr_3 within the pores. However, new well-defined excitonic peaks appear at 427 nm and at 432 nm for APbBr_3 @nano-Cr-MIL-101 ($\text{A} = \text{Cs}$, FA , respectively) (Figure 4b). These correspond to 3 nm CsPbBr_3 (440 nm) and FAPbBr_3 (450 nm) photoluminescence peaks. For 3 nm MAPbBr_3 @nano-Cr-MIL-101, the emission peak maximum is at 446 nm (Figure S7). The lifetimes of the excited states are 1.5 ns (CsPbBr_3) and 2 ns (FAPbBr_3) at room temperature (Figure S12), in good agreement with predicted photoluminescence decay lifetimes for strongly confined CsPbBr_3 .³⁹

Tellingly, photoluminescence studies of CsPbBr_3 @nano-Cr-MIL-101 reveal an asymmetric peak defined by the morphology of the host itself. The ratio of 2.9 nm pores to 3.4 nm pores in pure Cr-MIL-101 is 2:1. Peak deconvolution in the emission spectrum revealed that the emission of QDs hosted in the 3.4 nm cages is red-shifted by 14 nm from the emission of the smaller QDs hosted in 2.9 cages (Figure S13).

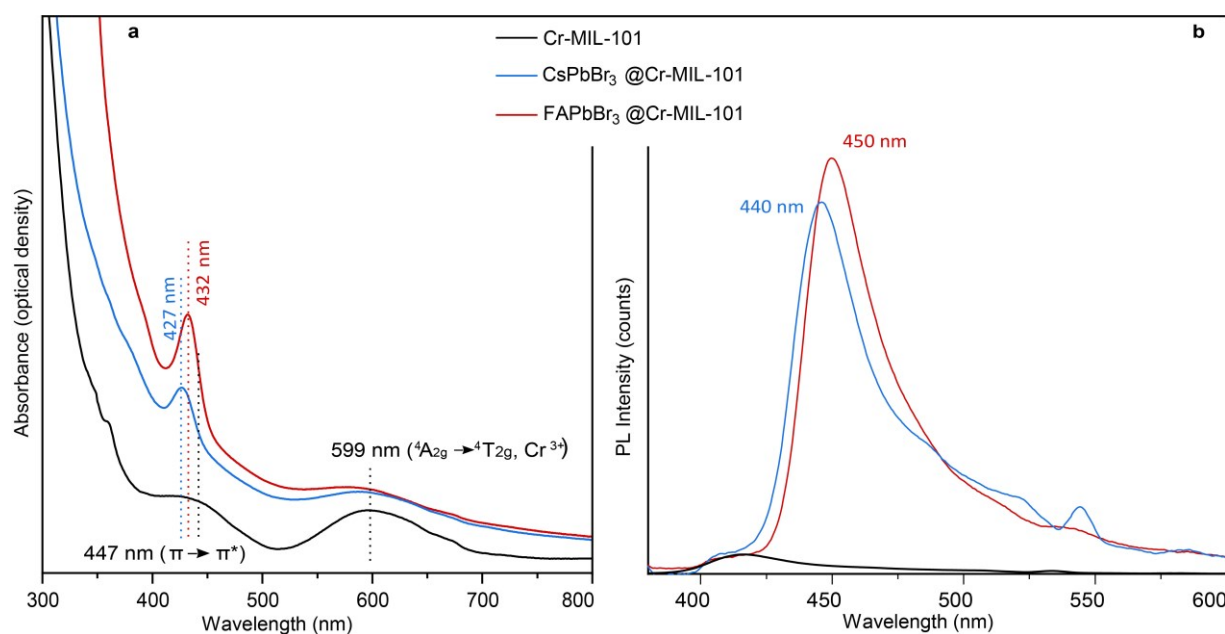


Figure 4. (a) Absorbance and (b) photoluminescence spectra for nano-Cr-MIL-101, CsPbBr_3 @nano-Cr-MIL-101, and FAPbBr_3 @nano-Cr-MIL-101.

Furthermore, variable-temperature (VT) experiments performed on films reveal energy transfer from the quantum

dots hosted in the 2.9 nm cages to those in the larger cages upon raising the temperature from 80 K to 300 K (Figure S14).



Energy transfer phenomena can only occur when the QDs are in close proximity, as might be expected in CsPbBr_3 @nano-Cr-MIL-101, and as reported for concentrated solutions of polydisperse NCs.⁴⁰ Importantly, the position of the photoluminescence peak for CsPbBr_3 did not change with temperature, confirming that the structure of the QDs remains constant over this temperature range and that QDs isolated within nano-Cr-MIL-101 retain the core structure of bulk CsPbBr_3 (γ -orthorhombic, $Pnma$). Conversely, for FAPbBr_3 @nano-Cr-MIL-101, with emission centered at 2.755 eV at room temperature, clear evidence of the $Pm\bar{3}m$ structure of the 3 nm QDs is given by the abrupt change of the peak position while cooling the sample from 300 K to 80 K. Bulk FAPbBr_3 itself transitions between 275 K and 250 K to a tetragonal $P4/mbm$ phase, which further distorts to the orthorhombic $Pnma$ phase between 150 K and 125 K.⁴¹ For the 3 nm FAPbBr_3 QDs isolated within nano-Cr-MIL-101, the phase transition between cubic and tetragonal occurs at slightly lower temperature (~ 250 K), as expected from the dramatic change in the material dimensions (from bulk to only 5–6 unit cells), while the orthorhombic $Pnma$ is observed below 150 K.⁴²

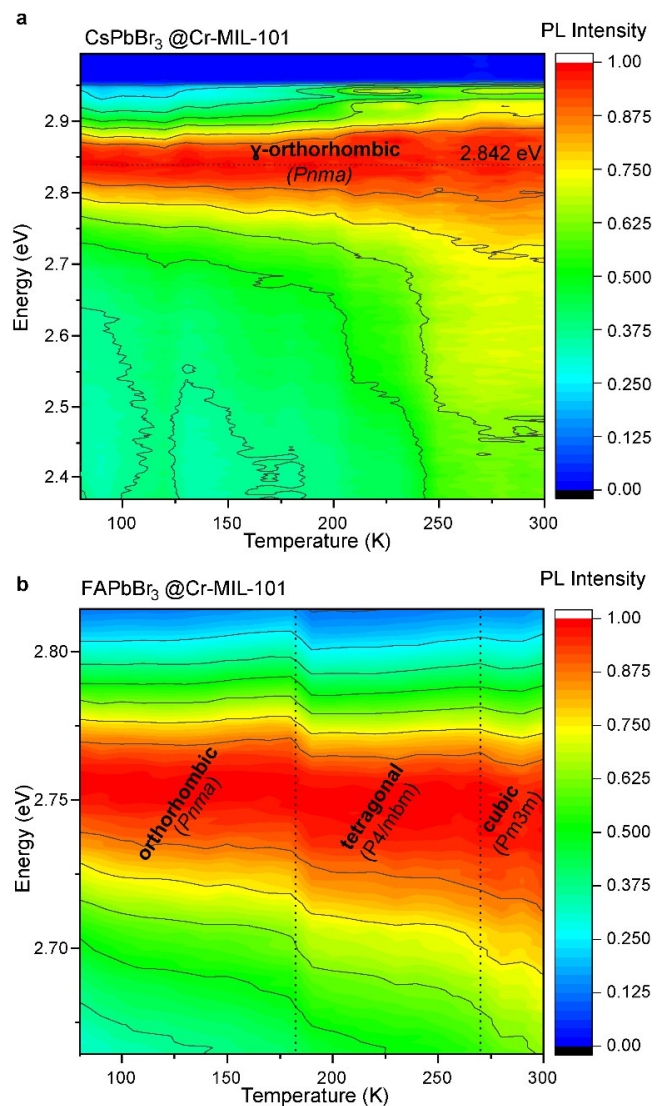


Figure 5. (a) Photoluminescence evolution over temperature (from 80 to 300 K) for CsPbBr_3 @nano-Cr-MIL-101. (b) Photoluminescence evolution over temperature (from 80 to 300 K) for FAPbBr_3 @nano-Cr-MIL-101.

The invariance of the APbBr_3 emission peak position over a wide range of temperatures informs on the influence of the MOF host on the optical properties of the perovskite QDs (Figure 5). Typically, LHP NPs exhibit a blue shift with increasing temperature.^{43,44} This behavior is similar to that of Pb chalcogenide QDs and is thought to originate from the interplay between thermal expansion and electron-phonon coupling. With increasing temperature, thermal expansion becomes a dominating factor for CsPbBr_3 because it decreases the interaction between the valence orbitals Pb 6s and I 5p. As a result, the forbidden gap increases, while the valence bandwidth narrows.⁴⁴ The fact that in APbBr_3 @nano-Cr-MIL-101, the main PL peak position is invariant with temperature for both Cs and FA analogs (excluding the change in the crystal structure for FAPbBr_3) confirm that the cages of the MOF constrain any lattice expansion with temperature (Figure 5b). The PL quantum yield of all investigated samples was invariably below 5%, which suggests an active interaction of the MOF with the LHP QDs leading either to the creation of traps on the surface of the QDs or to non-radiative recombination via photon emission. Note that the samples of APbBr_3 @nano-Cr-MIL-101 were synthesized, processed into films, and stored for more than 6 months in ambient atmosphere without changes in their optical signatures. However, accelerated degradation studies under continuous laser beam irradiation at 405 nm (40% humidity and 20 °C) highlight the limitations of the MOF host under external stimuli: 3 minutes of exposure leads to the formation of the 520 nm emissive structures, which indicate the degradation of the matrix and the formation of large, non-uniform particles (Figure S15).

To gain a more thorough understanding on the unusual effects of the host MOF onto the structure and behavior of the QDs trapped within the MOF cages, we performed massively parallel density functional theory (DFT) calculations on pristine Cr-MIL-101 and CsPbBr_3 , as well as a full model of the CsPbBr_3 @nano-Cr-MIL-101 composite. The smaller pore M cage of Cr-MIL-101 and a CsPbBr_3 NP of approximately 2.5 nm that perfectly fits into this cage were considered in a cluster approach (see the Supporting Information for full computational details). Geometries for the isolated systems were fully relaxed, and the density of states (DoS) for the minimum-energy structures of Cr-MIL-101 and CsPbBr_3 are shown in Figure 6. Analysis of the electronic structure indicates that the valence band (VB) of Cr-MIL-101 is localized on the inorganic cluster (primarily Cr d-electrons with additional contribution from the O and F p-electrons), whereas the conduction band (CB) is ligand-centered (delocalized frontier orbital over the terephthalate ligand; see Figure S16). The bandgap of Cr-MIL-101 in the spin-up channel (Cr-involved) is computed to be 2.51 eV (assigned to the experimental absorption band at 600 nm), and 3.17 eV in the spin-down channel (ligand-based, assigned to the experimental shoulder recorded at 447 nm) (Figure 6a and Figure S16a). For



the perovskite QDs, the VB is dominated by the Br p-orbital, whereas the CB belongs to the Pb p-orbital (Figure 6b, Figure S16b). Notably, we predict a bandgap of 2.83 eV for the 2.5 nm CsPbBr₃ QDs, which agrees well with the experimental absorption peak at 427 nm (2.90 eV). An embedding-inverted approach (nanoparticle atoms as monopoles) was used to analyze the effect of the perovskite nanoparticle onto the electronic structure of Cr-MIL-101 (see the SI for details). After taking into account for host-guest interactions through geometry relaxation, we find that both the VB and CB are slightly shifted to higher energy, with a negligible effect on the MOF bandgap itself (Table S2). More importantly, the frontier energy levels of Cr-MIL-101 and CsPbBr₃ in CsPbBr₃@Cr-MIL-101 (Figure S17) are well aligned, which may explain the efficient energy transfer between the two moieties.

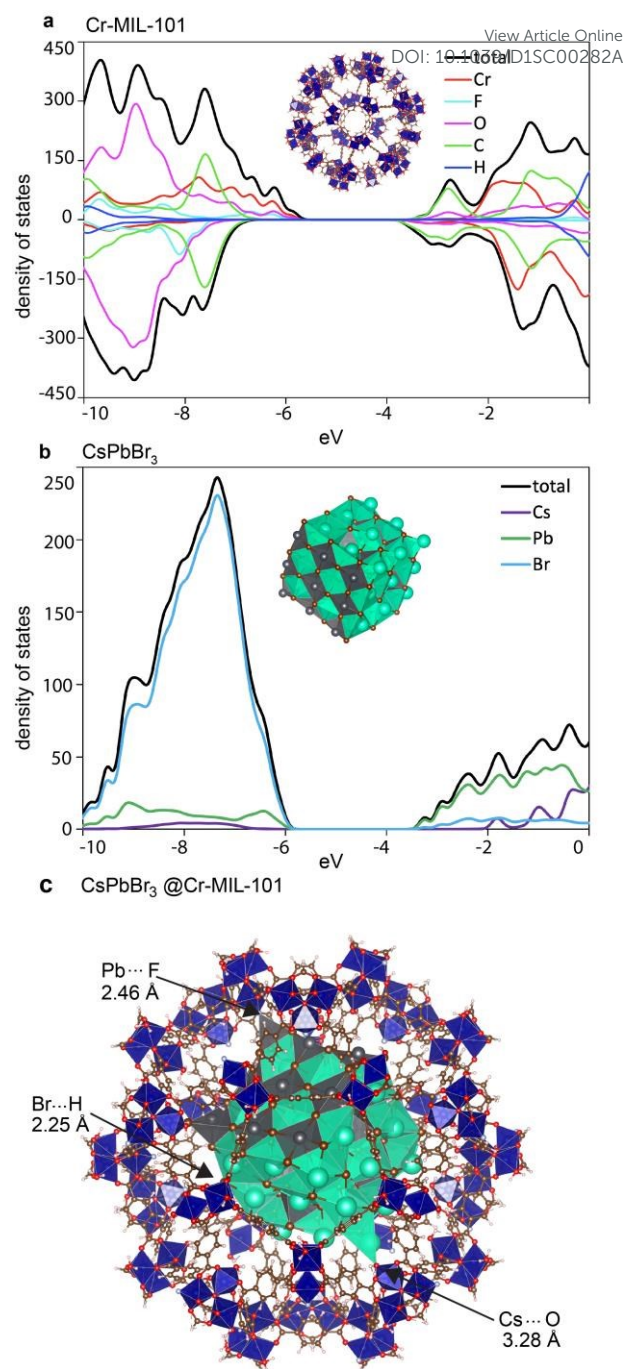


Figure 6. Electronic density of states calculated for (a) Cr-MIL-101 and (b) nano CsPbBr₃. (c) Minimum-energy geometry for CsPbBr₃@nano-Cr-MIL-101.

Evaluating the binding energy in the model CsPbBr₃@Cr-MIL-101 provided clues to the enhanced stability of the LHP QD within nano-Cr-MIL-101. Model optimization at the DFT level, including dispersion corrections, revealed strong interfacial interactions between the defectively-coordinated surface atoms of the perovskite nanoparticle and the inorganic coordination environment of the Cr-MIL-101 pore (Figure 6c). For instance, Cs...O (H₂O), Pb...F and Br...H (H₂O) contacts with short distances of 3.28, 2.46 and 2.25 Å, respectively, are observed in the minimum-energy structure (Figure 6c). These



interactions are likely to be responsible for the low PL quantum yield observed for CsPbBr₃ QDs inside the MOF. The binding energy, calculated as the energy difference between the minimum-energy of the composite and the constituting moieties, is predicted to be -232 kJ/mol, with approximately 50% contribution from long-range van der Waals dispersion interactions and 50% from electrostatic forces and short-range contacts. This large and negative binding energy explains the unusually high stability of the CsPbBr₃@nano-Cr-MIL-101 composite.

Conclusions

The foregoing results highlight the importance of nano-sizing the host itself in order to allow the crystallization/encapsulation and stabilization of ultra-small lead bromide perovskite QDs. Scaling down the particles of Cr-MIL-101 host to approximately 25 nm allows fast and efficient transport of LHP precursors within its pores and cages, which then enable the formation of 3 nm NPs of APbBr₃. These ultra-small QDs exhibit significantly blue-shifted emission peaks at 440 nm (Cs⁺), 446 nm (MA⁺), and 450 nm (FA⁺). Variable-temperature photoluminescence measurements exposed strong interfacial host-guest interactions that were confirmed by computational studies and are likely responsible for the unusual stability of the QDs, whose optical properties remain unaltered after months under ambient atmosphere. Our approach enabled the formation of the smallest LHP QDs yet and establish a blueprint towards the exploration of other perovskite nanostructures whose quantum confinement effects have not yet been explored at this scale. Equally intriguing for future studies are explorations of different MOF hosts with a diminished effect on the electronic level of the guest QDs.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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