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Mechanochemical Synthesis of Processable Halide Perovskite Quantum Dot-MOF Composite by Post-synthetic Metalation

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Perovskite quantum dots (PQDs) are some of the most sought after materials for optoelectronic and photovoltaic applications. We report the mechanochemical, solvent-free synthesis of PQD@MOF composite using a post-synthetically Ph∥ MOF AMOF-1 metalated anionic $\{[(NH_2Me_2)_2][Zn_3(L)_2].9H_2O\}$ (L=5,5'-(1,4phenylenebis(methylene))bis(oxy)diisophthalate) as template. CsPbX₃ PQDs are formed on the surface of AMOF-1 just by grinding Pb"@AMOF-1 with CsX (X=Cl, Br and I). The PQD@AMOF composites are characterized using PXRD and TEM. The size of the PQDs thus formed is restricted by AMOF-1 thereby manifesting quantum confinement effect. The composites show narrow and intense emission bands typical of PQDs. The luminescent AMOF is exploited for Försters Resonance Energy Transfer (FRET) to the stabilized CsPbBr₃ PQDs. AMOF-1 also imparts superior stability and processibility to the PQDs manifested fabricating colour-tunable ink using which is by а the composite.

Introduction

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Over the past decade, colloidal nanocrystal halide perovskite quantum dots (PQDs) have emerged as supremely important materials for photovoltaic and optoelectronic applications.¹⁻⁴ The miniscule sizes of PQDs endow them with a variety of interesting features⁵⁻⁷ involving an intriguing surface chemistry, which are otherwise not observed in their bulk counterparts.⁸ Among these, cesium lead halide (CsPbX₃) perovskite nanocrystals (NCs) have gathered the attention of scientists because of excellent photovoltaic efficiency.^{5,9} Their high emission intensities and quantum yield, narrow emission bands and tunable band gaps by composition, size or morphology have made them perfect candidates for optoelectronic devices, e.g., LEDs, lasers or specific detection.¹⁰⁻¹¹ However, the use of these materials in practical applications is hindered by their poor stability when exposed to variable atmospheric conditions e.g., humidity, temperature or light.¹² This instability can be majorly attributed to the ionic character of CsPbX₃ NCs along with their labile surfaces and metastable structures.¹³⁻¹⁴ In order to address this issue, besides the conventional method of synthesizing these NCs like hot injection and various liquid phase methods,¹⁵⁻¹⁷ attempts have also been made to immobilise them in silica or polymer matrices.¹⁸⁻²¹ The size and spatial control of such PQD

NCs by confining them within the nanospaces of a porous Metal-organic framework (MOFs)²²⁻²⁴ is an intriguing technique to tune their optical band gap while enhancing their stability.^{20,25-30} MOFs, well known for their porosity, tunability and high surface area, surpass contemporary porous materials in their flexibility and easy functionalization.²³ The regular structure of MOFs is particularly advantageous in quantum confinement of such NCs, thereby enhancing their optoelectronic properties, and providing extra stability for better performance in devices.²⁵⁻³⁰ There are only a handful of reports of PQD@MOF composites and the synthetic methods all involve harsh conditions concerning expensive and precarious organic solvents. and capping agents organometallic complexes. In a recent report, Zhang, et al. have derived PQDs from a Pb^{II}-based MOF.²⁵ However, the MOF template cannot sustain the harsh synthetic procedure and is broken down in the process. In contrast, a mechanochemical method would be simple, fast, efficient and environmentally benign for synthesizing such PQD@MOF composites.³¹⁻³⁴ However, attaining PQDs bv such mechanochemical methods is a highly challenging task owing to the lack of control over crystal growth. Moreover, the instability of the PQDs also demands synthesis in controlled and inert atmosphere.^{5,31-34} A porous template like MOF can alleviate this issue by restricting the size of the NCs and also by providing extra stability.

This work demonstrates the synthesis and characterization of unique $CsPbX_3@MOF$ composites by a simple mechanochemical grinding method involving a post-synthetically Pb^{II} metalated anionic MOF (AMOF). This process ensures the stabilization of PQD on the MOF surface, thus restricting their size and dictating their optical properties based on quantum confinement effect. The CsPbX₃@AMOF

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[#]Dedicated to Prof. C. N. R. Rao on the occasion of his 86th birthday.

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Scheme 1. Mechanochemical synthesis of ${\bf PQD} \textcircled{OMOF}$ composites mediated by ${\bf Pb^{II}}$ exchanged AMOF-1.

composites show intense luminescence, enhanced stability, processibility and also manifests energy transfer from the framework to the PQDs when X=Br. This is also the first report of (Förster Resonance Energy Transfer) FRET from the host luminescent framework to the stabilized CsPbBr₃ PQDs.

Experimental Section

Materials

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 $Zn(NO_3)_2.6H_2O$, dimethyl-5-hydroxy isophthalate, α, α' dibromo paraxylene, dibenzo 18 crown-6 and K_2CO_3 were all obtained from Sigma Aldrich Co. and were used as procured without further purification. All the solvents were obtained from Spectrochem Co.

Methods

Synthesis of $\{[(NH_2Me_2)_2][Zn_3(L)_2].9H_2O\}$ (AMOF-1)

AMOF-1 was synthesized according to a previous report.⁴⁰ $Zn(NO_3)_2.6H_2O$ (0.2 mmol, 0.059 g) and L (0.1 mmol, 0.047 g) were dissolved in DMF (6 ml), ethanol (3 ml) and distilled water (5 ml) in a 23 mL Teflon-lined stainless steel autoclave and was stirred for 30 minutes. The autoclave was sealed and was kept in an oven at 80 °C for 96 h. After completion of the reaction, the reactor was cooled at RT for 12 h. Colourless crystalline product was collected by filtration.

Synthesis of Pb^{II}@AMOF-1

AMOF-1 was degassed overnight at 120°C under vacuum. 150 mg of the degassed sample is then immersed in 5 ml 10^{-2} M solution of Pb(NO₃)₂ for a week and the solution is changed every alternate day. After a week, the residue wad centrifuged and washed several times with water to yield **Pb"@AMOF-1**. ICP-OES reveals that 18 wt% Pb is present in **Pb"@AMOF-1**, which is equivalent to 0.8 molecules of Pb" per formula unit of **AMOF-1**.

Synthesis of CsPbX₃@AMOF-1

3 equivalents of CsX are taken for 1 equivalent of Pb^{II} present in **Pb^{II}@AMOF-1**. Accordingly, 40 mg of **Pb^{II}@AMOF-1** was taken and 0.104 mmol of CsX was taken and grinded with **Pb^{II}@AMOF-1** in a mortar and pestle for 15-20 mins. The sample was intermittently checked under UV lamprifor the appearance of characteristic perovskite entities ion 039/C9TA05977F

Physical Measurements

The elemental analysis was carried out using a Thermo Fischer Flash 2000 Elemental Analyzer. Thermogravimetric analysis (TGA) was carried out using a Mettler-Toledo instrument in nitrogen atmosphere (flow rate = 50 ml min⁻¹) in the temperature range from 30 - 550 °C (heating rate: 3°C min⁻¹). Powder X-ray diffraction (PXRD) was recorded by using Cu-Ka radiation (Bruker D8 Discover; 40 kV, 30 mA). IR spectra of the compounds were recorded with a Bruker IFS 66v/S spectrophotometer using the KBr pellets in the region 4000–400 cm⁻¹. The scanning electron microscopy images were obtained using a Nova Nanosem 600 FEI field emission scanning electron microscope (FESEM). Transmission electron microscopy (TEM) analysis has been performed using a JEOL JEM-3010 with an accelerating voltage at 300 kV or a FEI TECNAI G2 20 STWIN TEM operating at 200 kV. One drop of the samples dispersed in ethanol solution was taken in a holey carbon coated Cu grid for TEM imaging. Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) measurements were recorded on a Perkin Elmer Optima 7000dv ICP-OES instrument. UV-Vis spectra were recorded on a Perkin Elmer Model Lambda 900 spectrophotometer. Fluorescence studies were accomplished using Perkin Elmer Ls Luminescence spectrometer. Time-resolved 55 decay experiments were recorded on a Horiba Delta Flex timecorrelated single-photon-counting (TCSPC) instrument. A 442nm nano-LED with a pulse repetition rate of 1 MHz was used as the light source. The instrument response function (IRF) was collected by using a scatterer (Ludox AS40 colloidal silica, Sigma-Aldrich). For the 442-nm LED light source, the instrumental full width at half maximum including detector response was 0.2 ns. The excited state decay of the sample was collected by fixing the emission wavelength at a particular wavelength. The decay was fitted using IBH software (DAS6).

Results and Discussions

Characterization of CsPbX₃@AMOF-1

In this work, we have chosen $\{[(NH_2Me_2)_2][Zn_3(L)_2].9H_2O\}$ (AMOF-1: L=5, 5′-(1,4-phenylenebis(methylene))bis--(oxy)diisophthalate), which is an 3D flexible AMOF, 35-40 with dimethyl ammonium (DMA) guest cations maintaining its charge neutrality. In **AMOF-1**, a trinuclear $[Zn_3(CO_2)_8]$ secondary building is connected by tetracarboxylate L linker to form the 3D network. In a previous report by us, AMOF-1 manifested excellent water stability, along with high affinity towards heavy metal cations like Pb^{II} by exchange with the guest DMA cation.40 We seek to transform the Pb^{II} encapsulated AMOF (Pb"@AMOF-1) into a value-added PQD@MOF composite by simple solvent-free means which will be ideal for several optoelectronic applications. The assynthesized AMOF-1 is desolvated under vacuum at 150°C in

Journal Name

Page 2 of 7

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order to remove water and DMF guests, after which it is immersed in a 0.1 M $Pb(NO_3)_2$ solution in water for a week. The solution is changed every day, in order to ensure maximum Pb^{II} loading. The sample thus obtained is washed with water several times to yield Pb"@AMOF-1, which contains 18 wt% Pb, as determined by ICP-OES. Accordingly, 3 molar equivalents of CsX (X= Cl, Br, I) are taken and grinded with Pb^{II}@AMOF-1 in a mortar and pestle without any solvent for 15 mins in the open atmosphere. When observed under UV lamp, the bright emission (blue when X=Cl, green when X=Br and red when X=I) starts appearing immediately with the grinding. The samples thus synthesized are characterized initially using powder X-ray diffraction (PXRD) where we clearly see the presence of perovskite peaks in addition to the peaks for AMOF-1 (Figure 1 (a,b)).⁴⁴ In each case, the low angle peak of **AMOF-1** is present at $2\theta = 5^\circ$. Since **AMOF-1** is a flexible MOF, the mechanical grinding may bring about orientational changes which are reflected by the appearances of some new peaks and change in intensities of the peaks in PXRD. These perovskite peaks have been matched with orthorhombic Pbnm phase in all three cases, which indicates that during mechanical synthesis, all of the CsPbX₃ PQDs crystallize in the orthorhombic phase. For comparison, we have (CsPbBr₃_mc) mechanochemically synthesized CsPbBr₃ without a template by grinding PbBr₂ and CsBr in the open atmosphere which also crystallized in the orthorhombic phase.⁴⁴ A previous report on the mechanochemical synthesis of CsPbX₃ has also recorded the formation of the perovskites in the orthorhombic phase.³¹ Thermogravimetric analysis (TGA) of CsPbX₃@AMOF-1 composites show high thermal stability by remaining unharmed till 280°C.44 The growing of the PQDs on

the MOF surface and corresponding blocking of the pore channels is also evidenced by the adsorption isotherm for CO₂ at 195 K, where CsPbBr₃@AMOF-1 shows a marked decrease in the total adsorption amount from AMOF-1.44 Under FESEM, AMOF-1 shows cuboidal microcrystallites which are 500-700 nm in length (Figure 1(c)). The PQDs stabilized on the MOF matrix were visualized using TEM, where well-defined quantum dots, 2-9 nm in diameter were observed uniformly distributed on rectangular MOF microcrystallites for CsPbCl₃@AMOF-1 (Figure 1(d)). HRTEM of a single PQD shows a lattice spacing of 0.301 nm, corresponding to (110) plane typical in orthorhombic CsPbCl₃ (Figure 1(e)). In case of CsPbBr₃@AMOF-1, the size distribution is similar and the PQDs show a lattice spacing of 0.298 nm, which corresponds to the (200) plane in orthorhombic CsPbBr₃ (Figure 1(f,g)).⁴¹ Similar morphology is also observed in case of CsPbl₃@AMOF-1, where a uniform distribution of PQDs of 5-8 nm dimensions is seen over the AMOF matrix.⁴⁴ In the absence of any template, CsPbBr₃ mc grows to large cuboidal nanocrystals, 100-200 nm in dimension without any uniformity in size (Figure 1(h)).31,44 However, in case of CsPbX₃@AMOF-1, confinement effect by the MOF surface supported by the post-synthetic cation exchange in AMOF-1 restricts the size of the PQDs to lower ranges of the nanoscale. Elemental colour mapping of CsPbX₃@AMOF-1 shows the presence of Pb, Cs and Cl/Br/I in the respective samples.⁴⁴ NC growth is restricted by AMOF, thereby controlling its size and it could be a prominent method to produce a library of CsPbX₃ PQDs. In order to demonstrate that homogeneous CsPbX₃ PQDs are not formed merely due to

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Page 4 of 7



300 400 500 0 10 20 30 40 50 Wavelength (nm) Figure 2 (a) UV-Vis Spectra of CsPbX₃@AMOF-1 and AMOF-1. (b) Photographs of solid samples of CsPbX₃@AMOF-1 (i: CsPbCl₃@AMOF-1; li: CsPbCl₅Br_{3-x}@AMOF-1 ; li: CsPbBr₃@AMOF-1; lv: CsPbBr₄l_{3-x}@AMOF-1; v: CsPbi₃@AMOF-1) under ambient and UV light. (c) Emission spectra of I-V. (d) Dispersions of CsPbBr₃@AMOF-1 nanccomposite. Green: Absorbance spectrum of CsPbBr₃@AMOF-1, Blue: Emission spectrum of AMOF-1; Pink and orange: Emission spectra of CsPbBr₃@AMOF-1 excited at 320 and 400 nm, respectively. (f) Fluorescence decay profiles for CsPbBr₃@AMOF-1 at different excitation wavelengths.

capping by the MOF ligand, we have prepared another batch of sample by grinding PbBr₂ and CsBr with the ligand L (CsPbBr₃_L). Under TEM, for CsPbBr₃_L, we observe large rectangular chunks of bulk perovskite along with a few dots which have a non-uniform size distribution. This is a clear indication that the intact AMOF template restricts the size of CsPbX₃ and provided extra stability and the PQDs are not formed due to capping by the ligand leached from the framework.⁴⁴

Optical Properties of CsPbX₃@AMOF-1

The optical properties of the **CsPbX₃@AMOF-1** have been studied extensively. The solid-state UV spectrum of **AMOF-1** shows absorption maximum at 316 nm and a blue emission with a broad emission peak centred at 420 nm. The optical

properties of Pb^{II}@AMOF-1 are identical to that of AMOF-1. However, in case of all the CsPbX₃@AMOF-1 samples, the individual absorption bands of the respective PQDs also appear with maxima at 401 nm when X = Cl, at 508 nm when X = Br and at 670 nm when X = I, in addition to the 316 nm band for AMOF-1 (Figure 2(a)). CsPbCl₃@AMOF-1 shows intense blue emission with emission maxima at 412 nm (λ_{ex} =320 nm) whereas CsPbBr₃@AMOF-1 shows a bright green emission with emission maxima at 515 nm when excited at 365 nm. The CsPbl₃@AMOF-1 shows red emission with emission maxima at 695 nm, when excited at 500 nm (Figure 2(b,c)). The emission bands are extremely narrow which indicates towards the narrow size distribution owing to quantum confinement.⁸ All the samples show typical intense luminescence under UV lamp in both solid states as well as when dispersed in ethanol (Figure 2(b,d)). When excited at 365 nm, CsPbBr₃_mc shows an emission peak with a maximum at 530 nm, which is very

broad due to the heterogeneity in size. Owing the size restriction of the PQDs by the AMOF, quantum continement effect is at play in the composites.⁴²⁻⁴³ This is established by the blue-shift in the emission maximum of **CsPbBr₃@AMOF-1** from that in **CsPbBr₃_mc** and the uniformity in size also ensures a sharp narrow peak.³¹ According to a calculation by Protesescu, *et al.*, the exciton Bohr diameter of the CsPbCl₃, CsPbBr₃ and CsPbl₃ are 5, 7 and 12 nm, respectively.⁸ In order to behave like a PQD, the semiconductor NCs should have diameters lower than their exciton Bohr diameter.⁸ Hence clearly, in case of **CsPbX₃@AMOF-1**, the nanocrystals which are 2-9 nm in diameter are indeed highly luminescent PQDs formed by the confinement effect of the AMOF.

Energy Transfer in CsPbBr₃@AMOF-1

The emission peak of AMOF-1 is a broad band with a maximum at 420 nm whose tail extends till 580 nm (Figure 2(e)). Hence it finds an overlap with the absorbance of CsPbBr₃, giving rise to the possibility of energy transfer from donor AMOF-1 host to PQD. True to our conjecture, upon exciting CsPbBr₃@AMOF-1 at 320 nm (absorbance MOF), the emission of the pristine AMOF-1 at 420 nm is almost guenched (Figure 2(e)), however it yields very high intensity emission peak with a maximum at 515 nm corresponding to CsPbBr₃. In addition, the direct excitation at 400 nm shows less intensity of the 515 nm peak compared to indirect excitation at 320 nm, clearly indicating a light harvesting phenomenon through FRET mechanism (Figure 2(e)). This is further supported by the excitation spectrum of the 515 nm peak of CsPbBr₃@AMOF-1 which shows a maximum at ~320 nm, clearly suggesting the contribution of MOF to the observed PQD emission.44 The transfer of energy from the framework to encapsulated CsPbBr₃ is also evident from the time-resolved photoluminescence decays of CsPbBr₃@AMOF-1. The original AMOF-1 emission at 420 nm shows a lifetime of 4.25 ns, which is reduced to 0.01 ns in CsPbBr₃@AMOF-1. Moreover, the 515 nm peak corresponding to acceptor CsPbBr₃ shows a lifetime of 7.97 ns when excited at 295 nm (Figure 2(f)). However, when excited directly at 370 nm, a shortening emission lifetime (3.3 ns) is observed, as compared to indirect excitation (Figure 2(e)).⁴⁴ The fluorescence lifetimes of the other samples were also measured and have been tabulated in Table S2.44 When excited at wavelength 295 nm, the 417 nm peak of CsPbCl₃@AMOF-1 shows an average lifetime of 6.11 ns and the 695 nm emission peak of CsPbl₃@AMOF-1 show a lifetime of 30.3 ns, when excited at 370 nm. CsPbCl₃@AMOF-1 records a quantum yield of 1.71%, whereas CsPbBr₃@AMOF-1 and CsPbl₃@AMOF-1 show quantum yields of 14% and 4.62% respectively.

In addition to CsPbX₃@AMOF-1, we have been also able to synthesize two intermediates CsPbCl_xBr_{3-x}@AMOF-1 and CsPbBr_xI_{3-x}@AMOF-1 which show emission maxima at 458 nm and 548 nm. respectively. CsPbCl_xBr_{3-x}@AMOF-1 is synthesized grinding CsPbCl₃@AMOF-1 by and CsPbBr₃@AMOF-1 together, whereas CsPbBr_xI_{3-x}@AMOF-1 is synthesized by grinding CsPbBr₃@AMOF-1 and CsPbl₃@AMOF-1 together. Since these are intermediate compounds that have been

Journal Name



Writing with Pb[®]@AMOF-1 Writing turns green emissive Figure 3(a) Photograph of dispersion of CsPbBr₃@AMOF-1 in different solvents under a UV light over several days. (b) Stability of emission of CsPbBr₃@AMOF-1 dispersed in different solvent over 14 days. (c) Colour tunability and easy processiblity in this composite material displayed by writing with a pen containing Pb[®]@AMOF-1 and then spraying it with CsBr.

prepared by grinding two different perovskites together, we have little control over the size and composition of the resultant PQDs. Hence owing to the heterogeneity in size and composition, they show very broad emission bands. We observed an interesting anion exchange feature as well, where CsPbBr₃@AMOF-1 upon grinding with CsI completely converts to CsPbI₃@AMOF-1, as evident from the complete conversion of the emission colour from green to red.⁴⁴ This indicates towards a facile anion exchange in case of the perovskite nanocrystals, assisting in easy inter-conversion and hence, colour-tuning.

Stability and Processibility of CsPbX₃@AMOF-1

One of the most important features of the CsPbX₃@AMOF-1 composites is their exceptional robustness owing to caging by the framework which makes them lucrative for several applications. The solvent stability of the composite material was tested by immersing the solid CsPbBr₃@AMOF-1 in different solvents over long periods of time while checking the emission intermittently. The emission intensity is found to be same in acetonitrile, toluene and dimethylformamide even after two weeks (Figure 3(a,b)).44 However, CsPbBr₃_mc loses its emission even when exposed to air for more than 24 hrs and its stability in the different solvents is only for a few hours.⁴⁴ This clearly elucidates that the strong binding of the PQDs on the AMOF surface provides them with superior stability in different media and thus they can be easily processable for a variety of applications. Although the emission is quenched immediately when CsPbBr₃@AMOF-1 is immersed in water, the framework remains intact and can be reused, as is evident from the PXRD pattern obtained after exposure to water. This is also an evidence that the formation of the PQDs do not disrupt the structural integrity of the framework.44

In order to illustrate the processibility and application of CsPbBr₃@AMOF-1, we attempted the development of a colour changing security ink exploiting the simple synthetic technique of the PQD@MOF composite and its supreme stability. We

dispersed **Pb^{II}@AMOF-1** in toluene and inserted it into the ink chamber of a roller ball pen (**Figure 3(c**)) and Wrote With 150775 piece of paper. This writing shows a pale blue emission under UV lamp. As soon as the writing is sprayed with a CsBr solution, the writing turns green emissive and conspicuous owing to the formation of CsPbBr₃. Hence this is a highly processable material which can be used for easy colour tunability and can find applications in security ink. The emission of the **CsPbX₃@AMOF-1** samples and the intermediates when plotted on CIE chromaticity covers a wide colour gamut.^{5,8,44}

Conclusions

In conclusion, in this work, we have demonstrated a simplistic green approach for the sustainable solvent-free synthesis of PQDs on an AMOF template with high stability and exciting optoelectronic properties. The Pb^{II} stabilized AMOF restricts the size of the QDs and determine their luminescent properties. Energy transfer is also observed from the framework to the stabilized CsPbBr₃ QDs. The AMOF template also renders supreme stability to the PQDs, making stable dispersion in a variety of solvents, thereby enhancing their processibility. This work is remarkable since it does not involve the several environmentally hazardous organic reagents traditionally used for the synthesis of halide perovskite quantum dots. Thus this method can be further used for the synthesis of a library of such composites for various specific applications owing to their intense luminescence and solvent stability.

Conflicts of interest

There are no conflicts to declare.

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Note

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6 | J. Name., 2012, 00, 1-3

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 CsPbX_3 perovskite quantum dots mechanochemically synthesized within an anionic MOF show intense luminescence and high solvent stability.