Supporting Information

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

Sohini Bhattacharyya*, Darsi Rambabu and Tapas Kumar Maji*

*Molecular Materials Lab, Chemistry and Physics of Materials Unit, School of Advanced Materials (SAMat), Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India.

Email: tmaji@jncasr.ac.in

Table of Contents

Experimental Section ................................................................................................................2
Synthesis of 5,5'-(1,4-phenylenebis(methylene))bis(oxy)diisophthalate ..................................2
Synthesis of 5,5'-(1,4-phenylenebis(methylene))bis(oxy)diisophthalic acid (L) ..................2
Synthesis of CsPbX$_3$@AMOF-1 .........................................................................................2
Synthesis of CsPbBr$_3$ mc ..................................................................................................3
Preparation of Colour-tunable Ink .......................................................................................3
Physical Measurements ........................................................................................................3
Preparation of Sample for Adsorption ................................................................................4
Characterization ....................................................................................................................5
Optical Properties ..............................................................................................................10
References ..........................................................................................................................16
Experimental Section

Synthesis of 5,5′-(1,4-phenylenebis(methylene))bis(oxy)diisophthalate

This compound has been prepared according to previous reports.1,2 A mixture of dimethyl-5-hydroxy isophthalate (10.0 mmol), α,α' dibromo paraxylene (4.96 mmol), dibenzo 18 crown-6 (0.277 mmol) and K₂CO₃ (2.21g, 16 mmol) were stirred in dry THF (40 ml) at 70°C for 24 hours. After this stirring 20 ml 10 % aqueous Na₂CO₃ solution was added at 0°C under an ice bath. The resulting white solid was filtered and washed with water for several times and finally with diethyl ether and dried under vacuum. Yield: 97% relative to dibromo paraxylene. ¹H NMR (400 MHz, CDCl₃): δ = 8.29 (s, 2H), 7.83 (s, 4H), 7.48 (s, 4H), 5.16 (s, 4H), 3.93 (s, 12H).

Synthesis of 5,5′-(1,4-phenylenebis(methylene))bis(oxy)diisophthalic acid (L)

A mixture of 5,5′-(1,4-phenylenebis(methylene))bis(oxy)diisophthalate (2 mmol), KOH (20 mmol), 40 ml MeOH and 40 ml distilled water were stirred at 80°C in oil bath for 24 hours. The reaction mixture was filtered to remove any unreacted starting materials and 30 ml 6(M) HCl was added dropwise to filtrate at 0°C under stirring. The white precipitate was filtered and washed with distilled water for several times and dried under vacuum. ¹H NMR (400 MHz, DMSO-d₆): δ = 13.29 (br, 4H), 8.05 (s, 2H), 7.69 (s, 4H), 7.47 (s, 4H), 5.21 (s, 4H).

Synthesis of CsPbX₃@AMOF-1

3 equivalents of CsX are taken for 1 equivalent of Pb⁺⁺ present in Pb⁺⁺@AMOF-1. Accordingly, 40 mg of Pb⁺⁺@AMOF-1 was taken and 0.104 mmol of CsX was taken and grinded with Pb⁺⁺@AMOF-1 in a mortar and pestle for 15-20 mins. The sample was intermittently checked under UV lamp for the appearance of characteristic perovskite emission.
Figure S1 Images captured during various stages during mechanochemical synthesis of CsPbI$_3$@AMOF-1 by mechanical grinding under UV light showing change from the blue emission of AMOF-1 to the red emission of CsPbI$_3$.

Synthesis of CsPbBr$_3$-mc

1 mmol each of PbBr$_2$ and CsBr were taken in a mortar and pestle and grinded for 15 mins in open atmosphere. A yellow solid was formed which was characterized by different techniques.

Synthesis of CsPbBr$_3$-L

1 mmol each of PbBr$_2$ and CsBr were taken in a mortar and pestle and grinded for 15 mins in the presence of 40 mg L ligand in an open atmosphere. A yellow solid was formed which was characterized by different techniques.

Preparation of Colour-tunable Ink

~50 mg of Pb$^{II}$@AMOF-1 was dispersed in 10 ml toluene and put inside the ink chamber of a roller ball pen. After writing with this pen, the writing portion was sprayed with CsBr solution in water to prepare CsPbBr$_3$@AMOF-1. The formation of this composite was easily realized by the green emission under UV lamp.

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	extsuperscript{-1}) in the temperature range from 30 – 550 °C (heating rate: 3°C min	extsuperscript{-1}). Powder X-ray diffraction (PXRD) was recorded by using Cu-K\textalpha 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	extsuperscript{-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 55 Luminescence spectrometer. Time-resolved decay experiments were recorded on a Horiba Delta Flex time-correlated single-photon-counting (TCSPC) instrument. A 442-nm 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).

**Preparation of Sample for Adsorption**

Adsorption isotherm of CO\textsubscript{2} at 195 K was recorded with the dehydrated sample using QUANTACHROME QUADRASORB-SI analyzer. To prepare the dehydrated sample of AMOF-1 and CsPbBr\textsubscript{3}@AMOF-1, approximately 100 mg of sample was taken in a sample holder and degassed at 150°C at 10\textsuperscript{-1} pa vacuum for about 8 h prior to measurements. The dead volume of the sample cell was measured using He of 99.999% purity. The amount of adsorbed gas was calculated from the pressure difference (\(P_{\text{cal}} - P_e\)), where \(P_{\text{cal}}\) is the calculated pressure with no gas adsorption and \(P_e\) is the observed equilibrium pressure. All operations were computer-controlled and automatic.
Characterization

Figure S3 (a) IR spectrum of AMOF-1. (b) IR spectra of CsPbX$_3$@AMOF-1 samples (X=Cl, Br & I).

Table S1: IR peaks in AMOF-1 and CsPbX$_3$@AMOF-1.

<table>
<thead>
<tr>
<th>Peak Position (cm$^{-1}$)</th>
<th>Nature</th>
<th>Vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>3460</td>
<td>broad</td>
<td>N-H stretch</td>
</tr>
<tr>
<td>3080</td>
<td>broad</td>
<td>=C-H stretch</td>
</tr>
<tr>
<td>1632</td>
<td>sharp</td>
<td>C=O stretch</td>
</tr>
<tr>
<td>1580</td>
<td>very sharp</td>
<td>C=C stretch</td>
</tr>
<tr>
<td>1370</td>
<td>very sharp</td>
<td>C-O-C stretch</td>
</tr>
</tbody>
</table>
Figure S4 PXRD of AMOF-1 and Pb$^{II}$@AMOF-1. (b) PXRD of AMOF-1 after being immersed in water for 7 days.

Figure S5 PXRD of AMOF-1 after being immersed in water for 7 days.
Figure S6(a) Thermal stability of Pb$^{II}$@AMOF-1 and CsPbX$_3$@AMOF-1 (X= Cl, Br and I) (b) CO$_2$ adsorption isotherms at 195 K for AMOF-1 and CsPbBr$_3$@AMOF-1.

Figure S7 PXRD pattern of CsPbI$_3$@AMOF-1.
Figure S8 TEM images of (a) CsPbCl$_3$@AMOF-1. (b) CsPbBr$_3$@AMOF-1. (c) CsPbI$_3$@AMOF-1.

Figure S9 Elemental colour mapping of CsPbCl$_3$@AMOF-1.
Figure S10 Elemental colour mapping of CsPbBr$_3$@AMOF-1.

Figure S11 Elemental colour mapping of CsPbI$_3$@AMOF-1.
Figure S12 Particle size distribution in (a) CsPbCl$_3$@AMOF-1, (b) CsPbBr$_3$@AMOF-1, (c) CsPbI$_3$@AMOF-1.

Optical Properties

Figure S13 Absorbance spectrum of CsPbBr$_3$ mc.
**Figure S14** Emission spectrum of AMOF-1.

**Figure S15** Conversion of CsPbBr$_3$@AMOF-1 to CsPbI$_3$@AMOF-1 by facile anion exchange.
**Figure S16** Excitation spectrum of CsPbBr$_3$@AMOF-1.

**Figure S17** Emission of the CsPbX$_3$@AMOF-1 samples plotted on a CIE chromaticity coordinates.
Figure S18 TCSPC lifetime plots for (i) CsPbCl$_3$@AMOF-1 (ii) CsPbBr$_3$@AMOF-1 and (iii) CsPbI$_3$@AMOF-1.

Table S2: Average lifetimes of CsPbX$_3$@AMOF-1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average Lifetime (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMOF-1; Ex. 295, Em. 420 nm</td>
<td>4.25</td>
</tr>
<tr>
<td>CsPbCl$_3$@AMOF-1; Ex 295, Em 417</td>
<td>6.11</td>
</tr>
<tr>
<td>CsPbBr$_3$@AMOF-1; Ex. 295, Em. 420 nm</td>
<td>0.01</td>
</tr>
<tr>
<td>CsPbBr$_3$@AMOF-1_Ex. 295, Em. 515 nm</td>
<td>7.97</td>
</tr>
<tr>
<td>CsPbBr$_3$@AMOF-1_Ex. 370, Em. 515 nm</td>
<td>3.3</td>
</tr>
<tr>
<td>CsPbl$_3$@AMOF-1_Ex. 370, Em. 695 nm</td>
<td>30.3</td>
</tr>
</tbody>
</table>
Figure S19 (a) PXRD, (b) PL spectrum, (c) TEM and (d) HRTEM of CsPbBr$_3$ mc.

Figure S20 Stability of CsPbBr$_3$ mc in different media.
Figure S21 PXRD pattern of CsPbBr₃@AMOF-1 after being immersed in water, which shows that the AMOF-1 framework is intact and can be reused.

Figure S22 TEM images of CsPbBr₃_L shows a mixture of bulk and quantum dot states.

Figure S23 Emission of CsPbBr₃@AMOF-1 after exposure to moist air.
References
