Linear assembly of lead bromide-based nanoparticles inside lead(II) polymers prepared by mixing the precursors of both the nanoparticle and the polymer

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Soranyel Gonzalez-Carrero,^a Lorena Bareño,^a Elke Debroye,^b Cristina Martin,^b Patricia Bondia,^c Cristina Flors,^c Raquel E. Galian,^a Johan Hofkens^{b,*} and Julia Pérez-Prieto^{a,*}

Mixing precursors of lead(II) polymers with those of lead bromide-based nanoparticles ($\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskites or PbBr_2), at room temperature and in the presence of cyclohexanemethylammonium bromide, generated colloidal nanocomposites which, when deposited on a hydrophobic surface led to long, form one-dimensional, ordered and well-defined architectures.

Lead halide perovskites present an APbX_3 formula, where A is a small organic cation, such as methylammonium (MA), formamidinium (FA) or cesium cation, X is a halide anion (Cl, Br and/or I) or a mixture of halides. Colloidal lead halide perovskites exhibit broad and intense absorption in the UV-VIS range, high photoluminescence and narrow emission, and solution-processability.¹⁻³ Their outstanding optical and electronic properties are motivating the use of APbX_3 nanoparticles not only in light emitting devices, solar cells and photodetectors, but also in sensing and photocatalysis.⁴⁻⁷ There is an increasing interest in the assembly of nanoparticles into superstructures with well-defined geometry to create new materials with potential novel applications.⁸⁻¹⁰ The assemblage of nanoparticles into one-dimensional (1D) ordered and well-defined architectures, two-dimensional (2D) membranes and close-packed three dimensional (3D) superlattices is usually driven by interactions between nanoparticles, such as Van der Waals forces, electrostatic and dipole-dipole interactions.¹¹ Colloidal nanoparticles can also be organized into ordered architectures by making use of template methods. In this way, colloidal nanoparticles, such as, CdTe, ZnO, silver, gold and lead halide perovskite nanoparticles have been assembled by using

biomolecules (DNA, proteins) and inorganic templates (nanowires and nanotubes) and external fields.¹²⁻¹⁶

Focusing on lead halide perovskites, and particularly on the formation of 1D, ordered superstructures, it has recently been reported that the co-assembly of pre-formed CsPbX_3 nanoparticles and lamellar ribbons, formed from the association of PbSO_4 -oleate clusters in hexane, eventually provides long and continuous 1D low-dimensional architectures.^{17, 18} To our knowledge, similar assemblies based on organic-inorganic hybrid lead halide perovskite nanoparticles have not been reported so far.

Unlike all-inorganic lead halide perovskite nanoparticles, hybrid lead halide perovskites can be efficiently prepared at room temperature by injecting a solution of the perovskite precursors (e.g., PbBr_2 , MABr and a medium-sized ammonium bromide salt) into a toluene. In addition, this year Rezvani et al.¹⁹ succeeded in preparing a 1D lead(II) coordination polymer with the formula $[\text{Pb}_2\text{L}_2\text{I}_4]_n$ (L: 1-methylimidazole), in which each L is coordinated to one Pb, using $\text{Pb}(\text{NO}_3)_2$, KI, and 1-methylimidazole as the polymer precursors.

Figure 1. Schematic representation of the new strategy for preparing ordered assemblies of MAPbBr_3 perovskites inside lead(II) coordination polymers: synthesis of colloidal MAPbBr_3 NP oligomers (1-3) and their transformation into 1D MAPbBr_3 nanoparticle polymers after their deposition on a carbon-coated Cu TEM grid and drying under hexane atmosphere.

^a Instituto de Ciencia Molecular (ICMoL), Universidad de Valencia, Catedrático José Beltrán 2, 46980, Paterna, Valencia, Spain.

^b Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001, Leuven, Belgium

^c Madrid Institute for Advanced Studies in Nanoscience (IMDEA Nanociencia), Faraday 9, 28049, Madrid, Spain

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Taking into account the mild conditions for the preparation of the hybrid perovskites and the possibility of forming 1D lead halide coordination polymers, we explored if injecting the mixture of all the precursors (both of the perovskite and the coordination polymer) into a low-polar solvent could provide ordered assemblies of lead halide-based nanoparticles, namely MAPbBr₃ perovskites, inside lead(II) coordination polymers.^{20,21-23} Here we describe, for the first time, the preparation of 1D assemblies of lead halide-based nanoparticles (PbBr₂ or MAPbBr₃) inside a lead bromide polymer, by concurrent formation of lead(II) oligomers and the nanoparticles in the presence of cyclohexanemethylammonium bromide (ChMABr) to lead to colloidal nanoparticle oligomers (Figure 1).

Deposition of the colloid on a carbon-coated copper TEM grid led to long, 1D, ordered and well-defined architectures; both the PbBr₂ and the MAPbBr₃ assemblies showed a high degree of linearity of several microns in length when they were dried under a hexane saturated atmosphere. By contrast, deposition of the MAPbBr₃ and PbBr₂ colloids on glass slides provided spherical aggregates, those arising from the former being smaller and more homogeneous (see below). The MAPbBr₃ assembly and its luminescence performance was studied in depth by using transmission electronic microscopy (TEM), scanning electron microscopy (SEM), correlative atomic force microscopy (AFM) and single particle fluorescence imaging, and fluorescence lifetime microscopy (FLIM).

With the focus on the preparation of assemblies consisting of lead halide perovskites inside a lead(II) polymer, we tested the combination of PbBr₂ in dimethylformamide (DMF) with different MABr:ChMABr molar ratios (Figure S1).²⁴ We describe here the most successful preparation. Briefly, a DMF solution containing PbBr₂, MABr, and ChMABr in a 1:0.93:0.07 molar ratio was added dropwise to toluene (5 mL) and stirred for 60 minutes at room temperature. The yellow colloidal solution was left to stand for 24 hours and then it was decanted. The precipitate (ca. 50% of the added material) consisted of bulk perovskite and was discarded.

The absorption spectrum of the supernatant showed the formation of a MAPbBr₃ colloid with an exciton peak at 523 nm (Figure 2a). The colloid exhibited photoluminescence (PL) with maximum at 530 nm (full width at half maximum, FWHM = 24 nm) and a PL quantum yield (Φ_{PL}) of 35% (Figure 2b). Time-resolved PL measurements showed a considerably long average lifetime (τ_{av} 769 ns) and the decay kinetics fitted to a three-exponential decay function (inset in Figure 2c, table S1).²⁵

The TEM and SEM images of the MAPbBr₃, deposited by drop casting of the colloid onto a carbon-coated copper grid surface and then dried under hexane atmosphere, showed the formation of bunches of 1D polymer-like chains of several microns in length, containing 7 nm-sized nanoparticles (7.2 ± 0.8 nm) with an average inter-particle distance of 7.0 ± 3.0 nm calculated from TEM images. Then, control assays were carried out in the absence of MABr under the same conditions. Remarkably, the deposition of the non-emissive colloid led to the formation of similar 1D polymer-like chains of several microns in length but containing PbBr₂ nanoparticles (Figure S2).

Figure 2. a) Absorption and b) normalized PL emission spectra of the MAPbBr₃ colloid. Inset image b: PL lifetime decay trace of the colloid. c) SEM and d,e) TEM images of the MAPbBr₃ colloid deposited on a carbon-coated TEM grid and dried under saturated atmosphere of hexane.

The powder X-ray diffraction (PXRD) and energy dispersive diffraction (EDS) spectra of the 1D MAPbBr₃ NP polymer were consistent with the formation of the perovskite cubic phase (*Pm-3m*) with an average Br:Pb ratio of 2.9, Figure S3.^{2, 26, 27} Additional studies for composition analysis were performed by using thermogravimetric analysis (TGA) and proton nuclear magnetic resonance (¹H-NMR), see experimental details in ESI. The TGA heating curve showed two weight losses at 329 °C (19 %) and 566 °C (81 %), attributed to the organic ammonium salts (MABr plus ChMABr) and PbBr₂, respectively (Figure S3).²⁸ The ¹H-NMR spectra revealed that the organic ligand ChMABr was present in the colloidal nanoparticles and not in the discarded

solid (Figure S4). Moreover, the X-ray photoelectron spectroscopy analysis the MAPbBr₃ NP polymer and that of the sample prepared in the absence of MABr, i.e., the 1D PbBr₂ NP polymer, Figure S5 and S6, confirm the presence of lead(II) in both polymers (see details of the analysis in ESI).

Attempts were made to obtain 1D ordered superstructures of MAPbBr₃ nanoparticles by drop-casting the colloid onto a hydrophobic glass slide followed by drying under a saturated hexane atmosphere with a view to obtaining information about their emissive properties (see experimental details in ESI). The AFM and SEM images (Figures 3 a-c) revealed a homogeneous distribution of a larger MAPbBr₃ nanomaterial (about 30 nm) that could have originated from the clumping of nanoparticle oligomers, from now onward termed as clumped MAPbBr₃ NP oligomers, MAPbBr₃ cNP_{oligomer}. This behaviour could be attributed to phobic interactions between the glass substrates and the colloid, Figures 3a, 3b and 3c. The inter-particle distance between the cNP_{oligomer} on the hydrophobic glass was estimated as 51 ± 23 nm from the SEM images (Figure S2 shows the analogous PbBr₂ cNP_{oligomer} from the control sample).

Even though the deposition of the MAPbBr₃ colloid on the hydrophobic glass could not be used to support the 1D nanoparticle polymer observed on the TEM grid, we turned our attention to investigating the PL features of the MAPbBr₃ cNP_{oligomer} sample. It showed an absorption and emission peak at 519 nm and 530 nm, respectively, Figure 3d (see details in the experimental section in ESI). It was possible to record PL of single cNP_{oligomer} by using correlative AFM and fluorescence microscopy, with laser excitation at 488 nm.^{29,30} The correlation showed that 90% of the individual MAPbBr₃ cNP_{oligomer} observed by AFM were emissive and characterised by strong PL intermittency or blinking (Figure S7). Considerable differences in intensity, frequency and duration of blinking were observed (Figure S7); a similar behaviour has previously been observed for MAPbI₃ and MAPbBr₃ crystals and films.^{31, 32} No clear dependence of the emission behaviour on the morphology and height of the MAPbBr₃ cNP_{oligomer} was observed. The PL intermittency in hybrid lead halide perovskite nanoparticles has been attributed to trap states, associated with chemical or crystal defects.³¹⁻³⁷ The PL decays of MAPbBr₃ cNP_{oligomer} collected from the FLIM images exhibited exponential decay kinetics that fit to a biexponential function (laser excitation at 488 nm, Figure 3e). The PL τ_{av} was 74 ns, with $\tau_1 = 14$ ns, $\tau_2 = 90$ ns (Figure S8, Table S2). Figure 3f shows the frequency histograms of the average PL lifetime obtained from the pixels analysed in different regions of the FLIM image. These regions exhibited a broad lifetime distribution centred at 100 ns. Similar results (τ_{av} of 100 ns; $\tau_1 = 16$ ns, $\tau_2 = 120$ ns) were obtained by conventional time-resolved PL spectroscopy measurements (light emitting diode excitation at 470 nm). The shortening of the PL τ_{av} and the fitting of the exponential decay kinetics to a biexponential function, instead of to a triexponential function as compared to the colloid, can be attributed to disassembling of the aggregates of NP oligomers (see Figure 1) when depositing them on the glass substrate.^{38,39}

Figure 3. (a,b) SEM images, (c) topographic AFM image, (d) absorption and emission spectra ($\lambda_{exc} = 470$ nm) and (e) FLIM image of the MAPbBr₃ colloid deposited on hydrophobic glass. (f) PL lifetime histograms collected from the selected area in image e. Scale bars: 2 μm (a), 300 nm (b), and 20 μm (e).

A double-layer light-emitting device based on the colloidal MAPbBr₃ nanoparticle oligomers in toluene (~ 40 nm) showed similar features to those previously reported for a device built from a MAPbBr₃ nanoparticle colloid,⁴⁰ with a turn-on voltage of 2 V and a narrow electroluminescence band centred at 534 nm (FWHM = 29 nm), Figure S9.

In summary, we report here the linear assembly of photoluminescent methyl ammonium lead bromide nanoparticles inside a lead(II) polymer by means of a simple and one-step method starting from the precursors of both materials and cyclohexylammonium bromide. This also applies to lead bromide; the assemblies are built under the same conditions but in the absence of methylammonium bromide. Deposition of the colloid on the hydrophobic surface of carbon-coated copper TEM grid led to long, 1D, ordered and well-defined architectures, while deposition of the colloid on glass slides provided spherical aggregates. The correlative single-particle fluorescence and AFM showed that ordered and non-connected MAPbBr₃ NP oligomers were mostly emissive and showed PL intermittency. The lifetime distribution of the ordered NP oligomers was narrow.

In future work we foresee the use of first-principles density functional theory calculations to understand all mechanistic aspects of the obtained assembly and, consequently, for designing new nanoparticles superlattices.^{41, 42}

Finally, this strategy could enable the linear assembly of perovskites with other functional nanoparticles to produce relevant hybrid systems.

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Conflicts of interest

There are no conflicts to declare.

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