

## Synthesis of New Perovskite Luminescent Nanoparticles in the Visible Range

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New large size luminescent nanoparticles have been prepared, based on lead bromide or iodide organic perovskites. The luminescent center is made of  $\text{PbX}_4^{2-}$  octahedrons. The preparation of the nanoparticles stems from fast nebulization and subsequent lyophilization of perovskite DMF solutions. The particles described have an average size of 60 nm, but a 20–500 nm range is in principle accessible. These new nanoparticles constitute an alternative to Q-dots which allows variable size while retaining the same emission wavelength, like silica particles functionalized with organic dyes, but with a higher stability under illumination.

### Introduction

Luminescent nanoparticles are nowadays raising a considerable interest due to their numerous applications in various fields such as sensing or LEDs. Up to now, three main categories of fluorescent objects have been described: quantum dots (Q-dots),<sup>1</sup> organic fluorescent nanocrystals,<sup>2</sup> and functionalized oxide (mainly silica) nanoparticles.<sup>3</sup> All these approaches suffer from some drawbacks. Organic dyes might present the disadvantage of moderate light resistance, although a recent report shows a noticeable improvement in the latter case.<sup>3c</sup> Q-dots are very stable under illumination but often blink. In addition, due to their very small size, their emission properties depend upon their size so that the polydisperse character of the Q-dots results in a broadening of the emission signal. Therefore there is still a need for

luminescent nanoparticles with tunable size while retaining a fair bleaching resistance and a constant emission wavelength.

It has been recently discovered that compounds of formula  $(\text{RNH}_3)_2\text{PbX}_4$  crystallize with a perovskite structure and can be cast or spin-coated into luminescent films onto various substrates.<sup>4,5</sup> The crystals are bidimensional and made of layers of lead tetrahalogenide octahedrons, where four bridging halogen ions participate to two octahedrons, each plan being taken between two ammonium layers.<sup>6–11</sup> A very stable exciton is formed upon light excitation,<sup>6,11,12</sup> and these inorganic systems are luminescent at ambient temperatures. Interestingly, Mitzi et al. have shown that perovskites are

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- (1) (a) Murray, C. B.; Kagan, C. R.; Bawendi, M. H. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545. (b) Bruchez, M., Jr.; Maronne, M.; Weiss, S.; Alivisatos, A. P. *Science* **1998**, *281*, 2013. (c) Chan, W. C.; Nie, S. *Science* **1998**, *281*, 2016. (d) Mattoussi, H.; Mauro, J. M.; Goodman, E.; Anderson, G. P.; Sundar, V. C.; Mikulec, F. V.; Bawendi, M. G. *J. Am. Chem. Soc.* **2000**, *122*, 12142. (e) Mandal, S. K.; Lequeux, N.; Rotenberg, B.; Tramier, M.; Fattacioli, J.; Bibette, J.; Dubertret, B. *Langmuir* **2005**, *21*, 4175.
- (2) Badré, S.; Méallet-Renault, R.; Dubuisson, E.; Ibanez, A.; Pansu, R. B.; Langhals, H. Presented at International Conférence on Photochemistry 2007, Cologne, Germany, 2007.
- (3) (a) Sanchez, C.; Lebeau, B.; Chaput, F.; Boilot, J.-P. *Adv. Mater.* **2003**, *15*, 1969. (b) Wang, L.; Tan, W. *Nano Lett.* **2006**, *6*, 84. (c) Ow, H.; Larson, D.; Srivastava, M.; Baird, B.; Webb, W.; Wiesner, U. *Nano Lett.* **2005**, *5*, 113.

(4) Ishihara, T.; Takahashi, J.; Goto, T. *Phys. Rev.* **1990**, *B42*, 11099.

(5) Parashkov, R.; Bréhier, A.; Georgiev, A.; Bouchoule, S.; Lafosse, X.; Lauret, J. S.; Nguyen, C. T.; Leroux, M.; Deleporte, E. Preparation and characterization of perovskite type semiconducting thin films. In *Advanced Materials: Research Trends (October 2007)*; Basbanes, L. A., Ed.; Nova Science Publishers: Hauppauge, NY, 2007; Chapter 12.

(6) Ishihara, T.; Takahashi, J.; Goto, T. *Solid State Commun.* **1989**, *69*, 933.

(7) Ishihara, T. In *Optical Properties of Low Dimensional Materials*; Ogawa, T.; Kanemitsu, Y., Eds.; World Scientific: Singapore, 1995; Chapter 6, p 288.

(8) (a) Mitzi, D. B.; Chondroudis, K.; Kagan, C. R. *IBM Res. Dev.* **2001**, *45*, 29. (b) Mitzi, D. B.; Prikas, M. T.; Chondroudis, K. *Chem. Mater.* **1999**, *11*, 542. (c) Mitzi, M. T.; Chondroudis, K. *Chem. Mater.* **1999**, *11*, 3028.

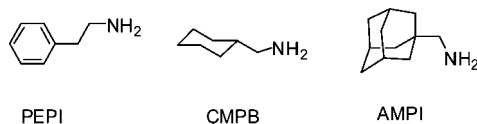
(9) Cheng, Z. Y.; Wang, Z.; Xing, R. B.; Han, Y. C.; Lin, J. *Chem. Phys. Lett.* **2003**, *376*, 481.

(10) Calabrese, J.; Jones, N. L.; Harlow, R. L.; Herron, N.; Thorn, D. L.; Wang, Y. *J. Am. Chem. Soc.* **1991**, *113*, 2328.

(11) Goto, T.; Ohshima, N.; Mousdis, G. A.; Papavassiliou, G. C. *Solid State Commun.* **2001**, *117*, 13.

(12) Tanaka, K.; Sano, F.; Takahashi, T.; Kondo, T.; Ito, R.; Ema, K. *Solid State Commun.* **2002**, *122*, 249.

Scheme 1



able to incorporate organic fluorophores that can tune their electrooptical properties like the anion provides in our case.

On the other hand, preparation of nanoparticles by spray-drying<sup>13</sup> (or nebulization/lyophilization) is a relatively good performing technique, which has been recently applied to nanoparticles preparation.<sup>14</sup> It is a very promising method, especially for robust compounds, which in addition can be easily scaled up if needed.

We report here the preparation and the characterisations of new nanoparticles prepared by the nebulization/lyophilization of  $\text{PbX}_4(\text{RNH}_3)_2$  ( $\text{X} = \text{I}$  or  $\text{Br}$ ) in dimethylformamide. The spherical nanoparticles obtained feature all the characteristics of the spin-coated or dip-coated films, with very little quantitative difference. They are very stable and highly crystalline and display fluorescence in the visible (blue and green) range.

### Experimental Section

The ammonium salt precursor of the perovskite was prepared by bubbling a flow of dry  $\text{HI}$  or  $\text{HBr}$ <sup>15</sup> gas into a dry ethereal solution of the amine. The following amines (Scheme 1) were used (Aldrich Chemicals) without purification. The names below refer to the corresponding perovskites in the paper (the last letter, I, standing for iodide and B for bromide). Solutions of perovskites were prepared by mixing stoichiometric amounts of the amine salt with the corresponding lead halide. 5% DMF solutions were used for the nanoparticles spray drying (see details below).

The experimental spray drier, shown in Supporting Information Figure 1, is composed of the aerosol generator (TSI 3076) from which drying droplets ( $0.35 \mu\text{m}$  initial mean diameter) are carried by dry air ( $3 \text{ L} \cdot \text{min}^{-1}$ ) into an evaporation chamber settled in an oven heated at  $250^\circ\text{C}$ . Dried particles are then collected onto a  $0.2 \mu\text{m}$  cutoff Teflon filter and stored as made at ambient temperature.

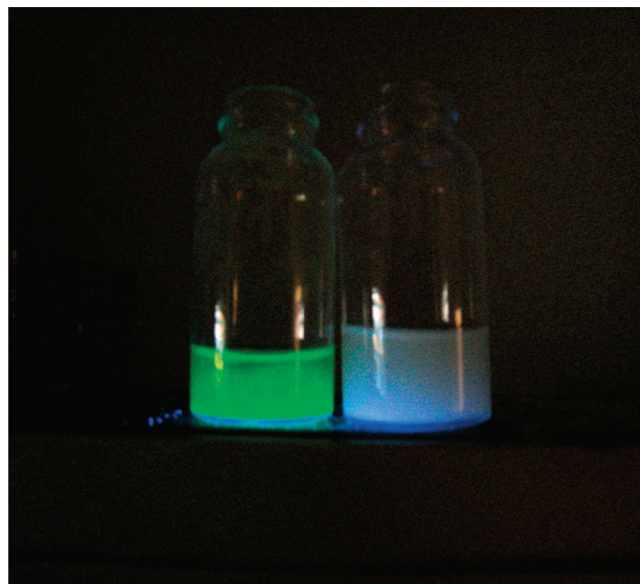
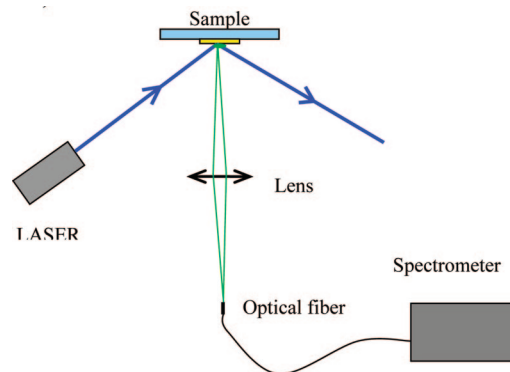
X-ray diffraction (XRD) data were collected with a D8 diffractometer from Bruker instruments (wavelength  $0.154 \text{ nm}$ ) between  $2$  and  $12^\circ$  in  $2\theta$  configuration. Transmission electronic microscopy (TEM) imaging was done with a CM-12 Philips ( $120 \text{ kV}$  acceleration).

The photoluminescence (PL) spectra of the particles were obtained with the apparatus described in Scheme 2 below, and the excitation was made through a laser diode at  $405 \text{ nm}$  (for iodide based perovskites) or a He–Cd laser at  $325 \text{ nm}$  (for the bromide based perovskite).

### Results and Discussion

The synthesis of the nanoparticles occurs readily as previously described for some oxides. The advantage of this

Scheme 2. Scheme of the Photoluminescence Setup



**Figure 1.** Luminescence of the nanoparticles dispersed in hexane: left,  $\text{PbI}_4(\text{PhCH}_2\text{CH}_2\text{NH}_3^+)_2$ ; right,  $\text{PbBr}_4(\text{CyCH}_2\text{NH}_3^+)_2$ .

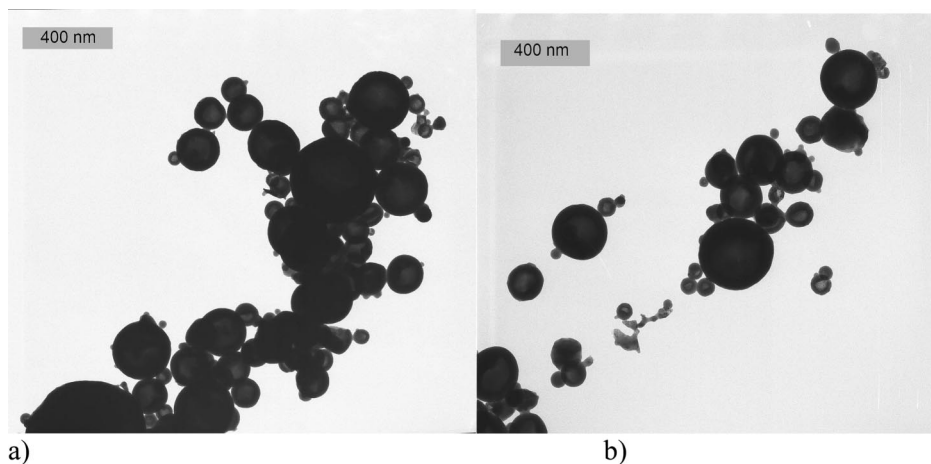
method is that it requires neither a special procedure nor toxic additives like phosphines. A limited amount of nanoparticles was produced because of the size of our equipment and the necessity to use not too concentrated solutions, but in principle nothing opposes scaling up the preparation. The particles are colored (pale yellow for bromide, orange for the iodide), and the colors are relatively close to the one of the corresponding lead halogenide. The particles exhibit an intense luminescence at ambient temperature, as pictured on the Figure 1 below.

The TEM pictures in Figure 2 show that all the particles are spherical as expected but somewhat polydisperse; the sizes are of the order of  $50$  to  $500 \text{ nm}$ , and a histogram of the size/proportion relationship can be determined by counting from any of the TEM pictures. The polydisperse character of the particles is due to the polydisperse character of the sprayed droplets. The size dispersion diagram of both the droplets (from the company) and the nanoparticles (from counting on pictures) is depicted, for example, for CMBP (Supporting Information Figure 1). It is clear that diagrams of identical shapes are obtained in both cases. In addition, the average size of the droplets is  $0.35 \mu\text{m}$ , while the nanoparticle average diameter of  $60 \pm 10 \text{ nm}$  has been determined. From the concentration  $C$  (in  $\text{g}/\text{cm}^3$ ) in solution

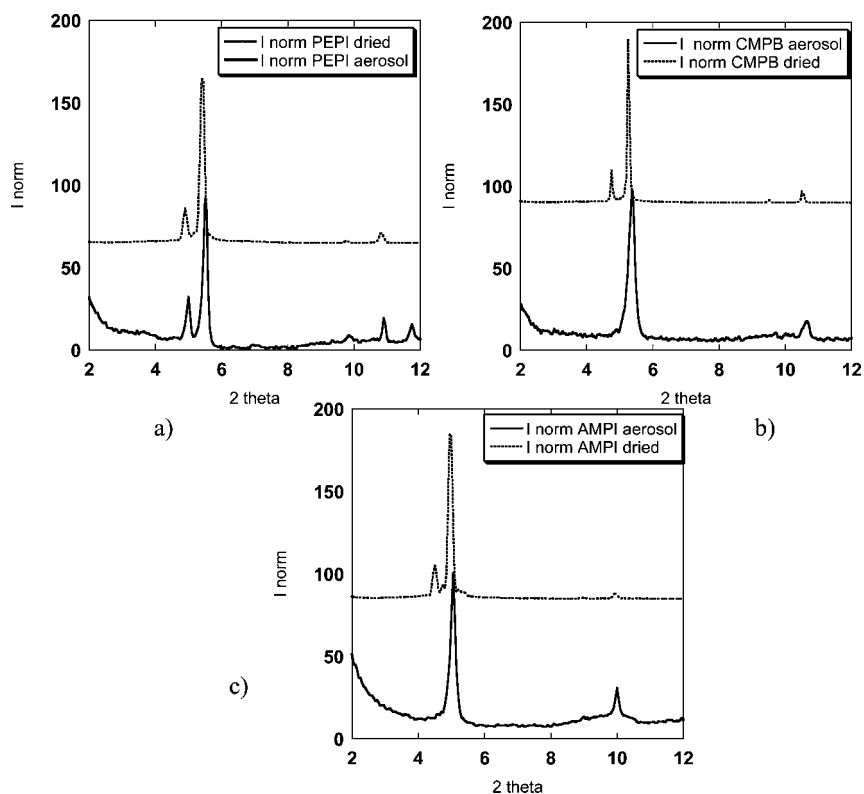
(13) Kodas, T. HampdenSmith, M. *Aerosol processing of materials*; Wiley-VCH: New York, 1999.

(14) Shanmugam, S.; Gabashvili, A.; Jacob, D.; Yu, J.; Gedanken, A. *Chem. Mater.* **2006**, *18*, 2265.

(15) The dry  $\text{HX}$  gases were prepared by dropping concentrated commercial acid (Aldrich) on phosphoric anhydride, an acidic very strong non-oxidizing dehydrating agent as previously described (Shevchenko, S. M. *Croat. Chim. Acta*, **2000**, *73*, 831). The gas was considered as dry enough for bubbling into the ethereal amine solution.



**Figure 2.** TEM pictures of the nanoparticles (a) AMPI and (b) CMPB. The hollow character of large particles is quite apparent in (b).



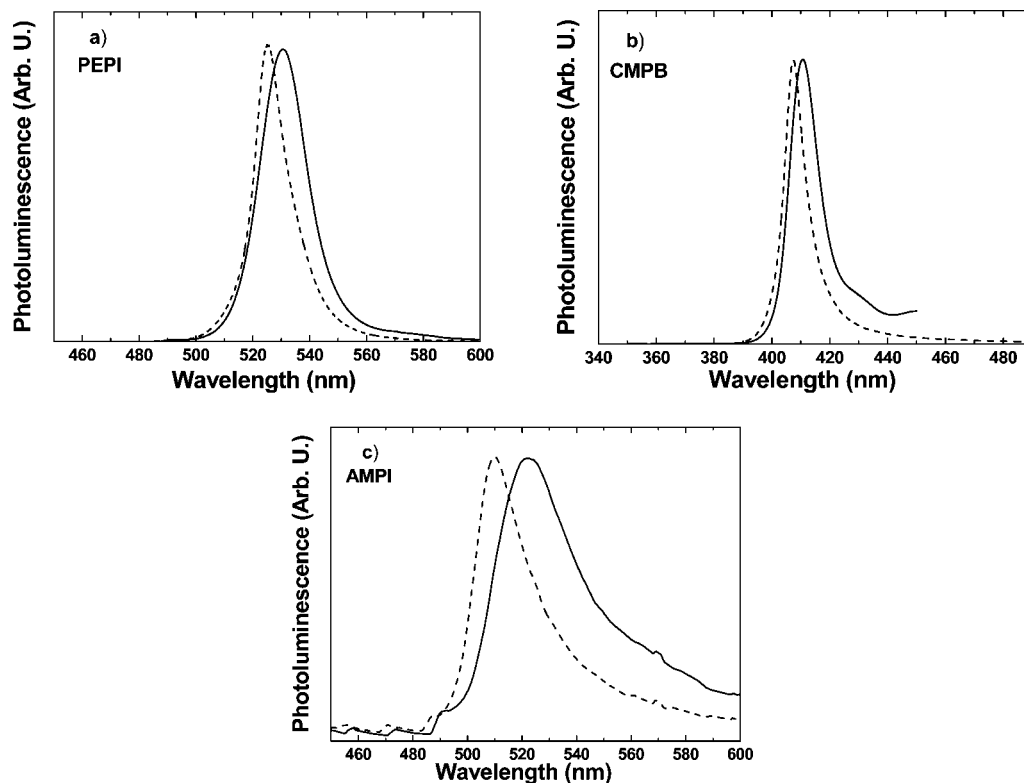
**Figure 3.** X-Ray diffraction spectra of the (a) PEPI, (b) CMPB, and (c) AMPI perovskites. The full lines correspond to the spectra of the nanoparticles and the dotted lines to the spectra of a bulk sample dried in the air.

and the density  $d$  of the solid, a ratio of the diameters equal to  $(C^{1/3})/d$  is to be expected between the droplets and the particles.  $C = 0.05 \text{ g/cm}^3$  and taking  $d \sim 3$  for a bromide perovskite (this estimated value being coherent with the order of magnitude found in ref 16) leads to a value of 0.13, which is in good agreement with the measured ratio of 0.17.

The particles also present an interesting feature: small particles are dense while larger ones are hollow, due to crystallization of the perovskite at the particle periphery while the middle of the drop underwent a depletion of the compound. With small particles, the drying was so fast that the process did not have time to occur. This phenomenon

can explain the small discrepancy between the estimated and the measured ratio between the size of the particles and the size of the droplets.

**Structural Characterization.** The X-ray diffraction spectra of the nanoparticles in Figure 3 show that the particles are fully crystalline. In the case of AMPI and CMPB based nanoparticles, a single crystalline phase is observed, showing therefore the high degree of organization of these particles. In the case of PEPI based nanoparticles, mainly one phase is observed, even though a very small additional peak exists aside, which could be attributed to the presence of another phase. Figure 3 shows also the X-ray spectra of the bulk samples dried in the air: a very small additional peak can be seen in each



**Figure 4.** Photoluminescence spectra of the three nanoparticles samples (solid lines) and of the spin-coated layers (dashed lines) obtained with the three perovskites (a) PEPI, (b) CMPB, and (c) AMPI. The excitation wavelength is 325 nm for AMPI and CMPB based samples and 405 nm for PEPI based samples. The PL curves have been normalized with their respective maximum intensities. The photoluminescence excitation spectrum of CMPB has been realized for a detection wavelength of 420 nm and is reported in Figure 2, Supporting Information.

spectrum, suggesting that the bulk samples display mainly one crystalline phase but can be weakly polluted by another phase. The X-ray spectra of the PEPI bulk sample and PEPI based nanoparticles are quite comparable to the ones of PEPI spin-coated layers we have performed or we can find in the literature<sup>8,9,17</sup> and also to X-ray spectra performed in a single crystal of PEPI,<sup>10,18</sup> where the layer spacing of the PEPI perovskite is found to be 1.6 nm.

**Optical Properties.** Figure 4 reports the photoluminescence spectra of the three nanoparticle samples. For CMPB based nanoparticles, the maximum of the luminescence is observed at 411 nm, while the maximum of the absorption occurs at 408 nm, providing a small Stokes-shift value of 3 nm. This value of the Stokes shift is quite coherent with the Stokes shift value of 4 nm we have measured in a CMPB spin-coated layer. Additionally, we have reported in Figure 4 the PL spectra of the self-assembled thin layers obtained by spin-coating the three perovskites on a glass substrate. It can be seen that the nanoparticles and the thin layers emit in the expected range: only a very slight wavelength shift of several nanometers is observed between the PL maximum energy positions of the nanoparticles and of the spin-coated layers. It is also worth noting that the full width at half-maximum (fwhm) of the photoluminescence (PL) peaks of the nanoparticles and of the spin-coated layers are of the same order of magnitude. All these observations lead to the conclusion that the optical characteristics of the nanoparticles

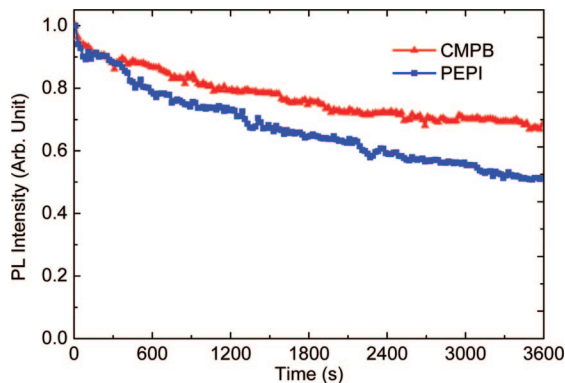
do not depend on their size. Following Ishihara et al.,<sup>4,6,7</sup> the bidimensionnal perovskite spin-coated layers form a crystal which presents a multiple quantum well electronic structure, having a period of 1.6 nm: the quantum wells consist of lead tetrahalogenide octahedrons monolayers (thickness around 0.6 nm), and the barriers consist of the organic alkylammonium layers (thickness around 1 nm). The excitons are strongly localized in the quantum well layers, that is, in the  $\text{PbX}_4^{2-}$  octahedrons, and their Bohr radius is about 1.7 nm.<sup>19</sup> The size of the nanoparticles, from 50 to 500 nm, is large compared to the Bohr radius of the excitons so that the optical properties of each nanoparticle are dominated by the optical properties of the crystal. The X-ray spectra confirm this fact as we have seen previously that the X-ray spectra of the nanoparticles are quite similar to the ones of the spin-coated layers or of the bulk samples. As a consequence, we can deduce from our PL and X-ray measurements that each nanoparticle is a small crystal having a bidimensional perovskite structure, emitting at a wavelength which does not depend on the size of the nanoparticle.

Nevertheless, we have observed that a slight wavelength shift of several nanometers is observed between the PL maximum energy positions of the nanoparticles and of the spin-coated layers. These differences can be assigned to different strain states inside the samples. Indeed, the nanoparticles and the spin-coated layers have not been grown in the same conditions. Additionally, the boundary conditions are very different between the two kinds of samples. In

(17) Hattori, T.; Taira, T.; Era, M.; Tsutsui, T.; Saito, S. *Chem. Phys. Lett.* **1996**, 254, 103.

(18) Ishihara, T. *J. Lumin.* **1994**, 60, 61–269.

(19) Hong, X.; Ishihara, T.; Nurmikko, A. V. *Phys. Rev.* **1992**, B45, 6961.



**Figure 5.** Photoluminescence spectra of CMPB (triangles) and PEPI (squares) based nanoparticles as a function of lightening time. The excitation wavelength is 325 nm, the intensity of the laser is  $50 \text{ mW} \cdot \text{cm}^{-2}$ .

inorganic semiconductor crystals, it is well-known that different growth conditions and different boundary conditions induce distortions and different strain states, inducing some changes in the electronic structure,<sup>20</sup> so that PL energy positions are slightly modified.

In order to test the stability of the nanoparticles under light, the evolution of the photoluminescence signal has been recorded as a function of illumination time in Figure 5 for CMPB and PEPI based nanoparticles. After 1 h, it is seen that the photoluminescence signal is reduced by a factor of 50% for PEPI nanoparticles, while it is only a factor of 30% for CMPB nanoparticles. This is in contrast with the bleaching of pure organic dyes which can occur within less than 1 s in some cases.<sup>21</sup>

## Conclusion

We have demonstrated for the first time the possibility to produce fluorescent hybrid nanoparticles from perovskite solutions. While the particles are still polydisperse, it should be possible to render them monodisperse by using a spray able to generate monodisperse droplets, and this will be the topic of future investigations. They, however, display a fluorescence which is only related to the particle composition as it could be expected. The perovskites are likely to be more photostable than free organics; moreover, they do not blink like quantum dots. Despite that their dispersion in water is still questionable, it might be possible that they can provide an alternative in several applications like bioimaging or sensing devices.

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**Supporting Information Available:** Scheme of the apparatus used for spray drying the nanoparticles, average size and distribution of both the nanoparticles and the droplets size, and photoluminescence excitation spectrum of CMPB perovskite nanoparticles (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

(20) Gil, B.; Briot, O.; Aulombard, R. L. *Phys. Rev.* **1995**, *B52*, R17038.

(21) Saylor, J. R. *Exp. Fluids* **1995**, *18*, 445.