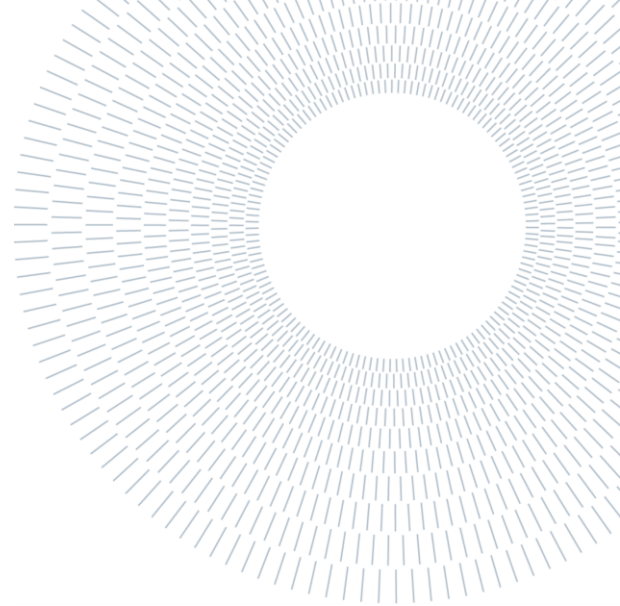




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EXECUTIVE SUMMARY OF THE THESIS

## Synthesis, Structural Characterization and Photophysical Properties of 1D Lead Halide Perovskites Based on Imidazolium Cations

TESI MAGISTRALE IN MATERIALS AND NANOTECHNOLOGY ENGINEERING

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### 1. Introduction

Hybrid lead halide perovskites (HPs) have gained considerable research interest over years due to their intriguing properties as semiconductors [1]. Their general formula  $ABX_3$  refers to cubic crystals, (Fig. 1a) where A is a monovalent organic cation, B an octahedrally coordinated metal cation (in this case lead) and X a halide anion ( $Cl^-$ ,  $Br^-$  and  $I^-$ ). Distortion from this cubic structure may arise due to size mismatch of cations and anions. The Goldschmidt tolerance factor  $\tau$  (eq.1 where  $r_a$  is ionic radius of organic cations and  $r_b$  and  $r_x$  are metal and halogen radius respectively) allows to partially predict stability and distortion of their crystal structure.

$$\tau = \frac{r_a + r_x}{\sqrt{2}(r_b + r_x)} \quad (1)$$

For cubic structures  $\tau$  is required to be  $0.8 < \tau < 1$ , which limits the choice of organic cation to  $CH_3NH_3^+$  (MA) and  $CH(NH_2)_2^+$  (FA). [1] Larger organic cations promote the formation of low-dimensional structures (Fig. 1).

Easy processing and tolerance to internal defects favored the studies of HPs for optoelectronic

applications with interesting results for solar cells and light emitting diodes. [1] However, the practical implementation of these materials is limited by a series of factors: lead toxicity, low stability due to degradation by air, moisture, light and defect present at surface and induced by undercoordinated species. [2] As an alternative, low dimensional perovskites (LDHPs) were studied. Their structure (Fig. 1 b, c and d) is composed of organic cations coordinated with lead halide octahedra isolated in clusters (0D perovskites) or connected in a sublattice continuous in two or one dimension (2D and 1D perovskite). [1]

LDHPs show improved environmental stability than 3D HPs thanks to barrier effect against oxygen and moisture offered by organic cations. [1] Moreover, alternating arrangement of organic and inorganic domains endows LDHPs with unique quantum and dielectric confinement effects as well different emission made from self-trapped exciton. Different levels of dimensionality can be achieved tuning cation's size and supramolecular interaction among organic and inorganic domains.

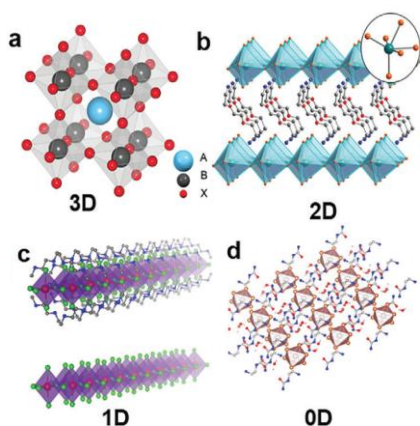


Fig. 1. Typical single crystal structures of organic-inorganic hybrid perovskites with different dimensionalities: 3D (a), 2D (b), 1D (c) and 0D (d)[1]

The presence of larger cations also affects connectivity inside lead halide sublattice as well as its distortion, thus impacting on electronic structure made from lead and halogen orbitals superposition. Bandgap can also be increased by level of quantum confinement that correspond to perovskite dimensionalities.[1]

Optical properties of LDHPs are affected by self-trapped exciton (STE), which creates additional emission minima with coupling between distortion of lead halide units and excited states. This effect results in a broad band emission with lattice deformation. 1D perovskites were investigated as phosphor for LED pumped from UV light thanks to their boarder STE emission made by easier distortion of lead halide chains.[1] However, these materials are relatively new and design guidelines must be defined in terms of structure-property relationship.[1]

Even though different cations and functional groups have been studied, conjugated cations with perfluoroalkyl chains have not been incorporated in perovskite yet. During my master thesis novel LDHPs containing imidazolium cations decorated with fluorinated chains have been synthesized and characterized, with the aim of controlling structures and tune photophysical properties of HPs by fluorination. Fluorination represents in fact a powerful tool to control physico-chemical properties and self-assembly behavior of materials. It is reported that, fluorination of A enhances performances of HPs as a result of the strengthening of the interactions with the inorganic framework. [3] This affects the connection modes of  $BX_6$  octahedra and their distortions and tilts, defining the bandgap

values.[3] Further, the hydrophobic barrier offered by fluorinated modules contributes to increase the stability.[2] 1-methyl-3-(3',3',4',4',4' pentafluorobutyl)imidazolium salts have been already used for surface passivation of perovskite solar cells, with interesting hydrophobic effect induced by fluorinated part.[2] Moreover, taking into account the high tendency to segregation of perfluorocarbons, i.e. *fluorophobic effect*, [4] we reasoned that introducing perfluoroalkyl chains could promote the formation of ordered structures. Different imidazolium cations with perfluoroalkyl chains of different length (Fig. 2) have already been synthesized and applied for the preparation of new LDHPs. Their effect on the structure and the photophysical properties of LDHPs has been analyzed in comparison with LDHPs containing 1-methyl-3-alkyl-imidazolium cations.

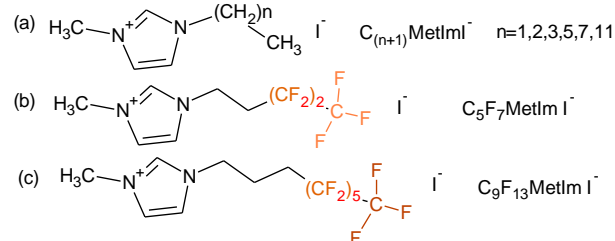


Fig. 2. Chemical structure of cations applied in the synthesis of LDHPs

## 2. Results and Discussion

LDHPs were synthesized by reacting imidazolium iodides (Fig.2) with  $PbI_2$  in 2:1 ratio, in HI aqueous solution (57%wt). Yellow crystals were obtained.  $C_2ImMet(PbI_3)$  and  $C_3ImMet(PbI_3)$  synthesis produces good quality single crystals. In both cases, X-ray diffraction revealed the presence of 1D perovskites with  $PbX_6$  octahedra connected in a face sharing mode (Fig. 3). Lead iodide chains are surrounded by cations with alkyl chain packed by hydrogen bonds within them and with halogens.

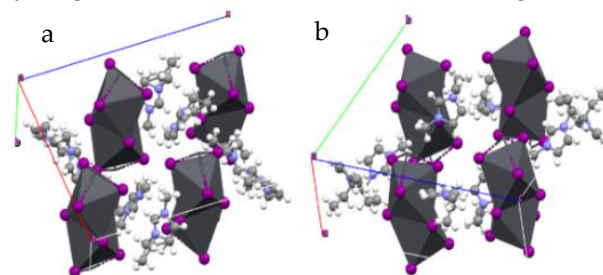


Fig. 3. Unit cells of (a)  $C_2ImMet(PbI_3)$  (orthorhombic) and (b)  $C_3ImMet(PbI_3)$  (monoclinic)

Powder XRD spectra (PXRD) were collected and a comparison with the simulated pattern from single crystals proved the presence of a single phase, coherent with single crystal structure and without impurities, as shown in Fig. 4.

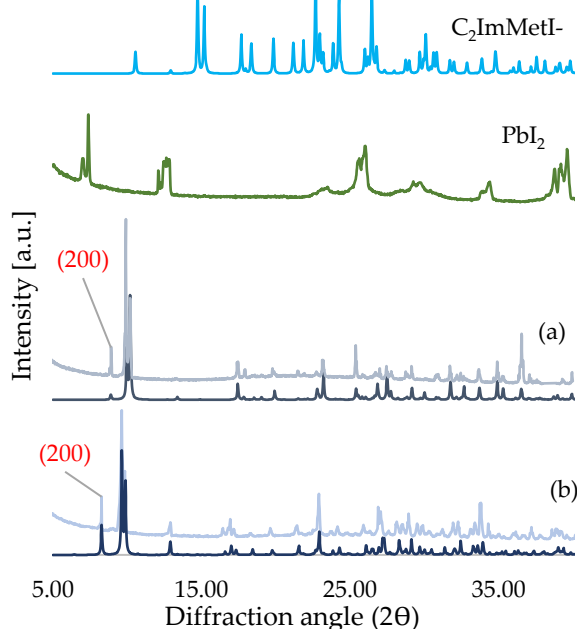


Fig. 4. Powder XRD comparison among  $\text{PbI}_2$ ,  $\text{C}_2\text{ImMetI}^-$  and lead iodide perovskite: (a)  $(\text{C}_2\text{ImMet})\text{PbI}_3$  and (b)  $(\text{C}_3\text{ImMet})\text{PbI}_3$  (simulated in blue experimental data in light blue, with (200) plane assigned)

Based on single crystal data, simulated PXRD planes parallel to lead iodide chains were assigned to peaks between  $5^\circ$  and  $15^\circ$ . According to results of lead bromide perovskite[5], plane (002) was set as reference, with peak at  $8.93^\circ$  for  $(\text{C}_2\text{ImMet})\text{PbI}_3$  and  $8.28^\circ$  for  $(\text{C}_3\text{ImMet})\text{PbI}_3$ . This shift is caused by a bigger unit cell induced by alkyl chain that results in a higher steric hinderance, as visible in Fig. 5. The same trend can also be observed for other peaks, as shown in Table 1.

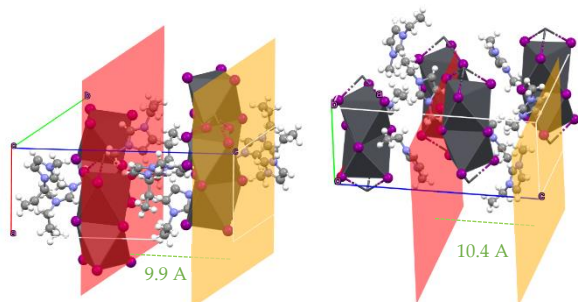


Fig. 5. (200) plane distance in  $(\text{C}_2\text{ImMet})\text{PbI}_3$  and  $(\text{C}_3\text{ImMet})\text{PbI}_3$  unit cells

Table 1. Peaks related to planes parallel to lead iodide chains

	Peaks at low angles (planes)
(a) $\text{C}_2\text{ImMet-PbI}_3$	8.93(002), 9.96(200), 10.2 (102)
(b) $\text{C}_3\text{ImMet-PbI}_3$	8.28(002), 9.65(012), 9.87(020)

FTIR analysis confirmed the cation incorporation into the inorganic framework. In fact, all the imidazolium salts show a single band in the region  $1500\text{-}1600\text{ cm}^{-1}$  associated to ring stretching vibrations. Upon reaction with  $\text{PbI}_2$  this band is split and a double peak appears at lower wavenumbers (green band of Fig. 6) due to different charge distribution induced by ionic interaction.[5,6] Moreover, the shift at lower wavenumbers of the N(1)-C(2)-H rocking ( $1100\text{ cm}^{-1}$ ) further confirms imidazolium incorporation (orange band of Fig. 6).[6] At wavenumbers higher than  $2800\text{ cm}^{-1}$ , CH stretching signals were observed, with shifts of  $\text{CH}_3$  ( $2900\text{ cm}^{-1}$ ) and C(2)-H ( $2800\text{ cm}^{-1}$ ) stretching at lower wavenumbers, upon reaction with  $\text{PbI}_2$  as shown in Fig. 7.

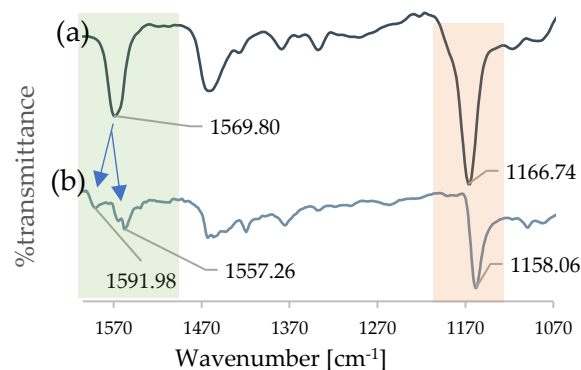


Fig. 6. FTIR spectra of (a)  $\text{C}_3\text{ImMetI}^-$  and (b)  $\text{C}_3\text{ImMet}(\text{PbI}_3)$  in typical imidazolium ring signals region

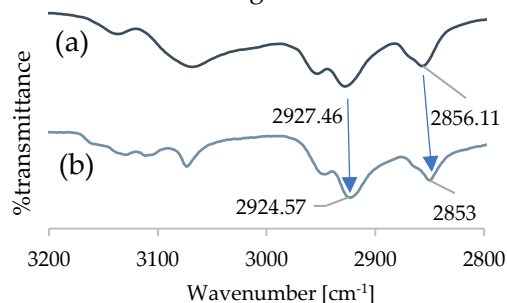


Fig. 7. FTIR spectra of (a)  $\text{C}_3\text{ImMetI}^-$  and (b)  $\text{C}_3\text{ImMet}(\text{PbI}_3)$  in CH stretching region

In the case of perovskites prepared with other  $\text{C}_m\text{ImMet}$  cations (with  $m > 3$ ), single crystal structures were not resolved, due to the increasing disorder induced by longer chains. However, FTIR

analyses show the same change of imidazolium stretching peaks confirming perovskite formation. In addition, PXRD patterns are similar to their lead bromide counterpart, suggesting 1D structure of obtained lead iodide perovskites [5].

Moreover, (002) plane shifted to lower angles increasing alkyl chain length (Fig. 8), as observed for  $C_m\text{ImMet}$  lead bromide. [5] This effect is due to longer alkyl chains and bigger cations that increase distance among lead halide chains and planes parallel to them. Therefore, it can be assumed a 1D structure for these perovskites, except for  $C_{12}\text{ImMet}$ , which shows an inversion point. This could probably be explained by considering the tendency to interdigitation of long alkyl chains, which reflect on interplane distances.

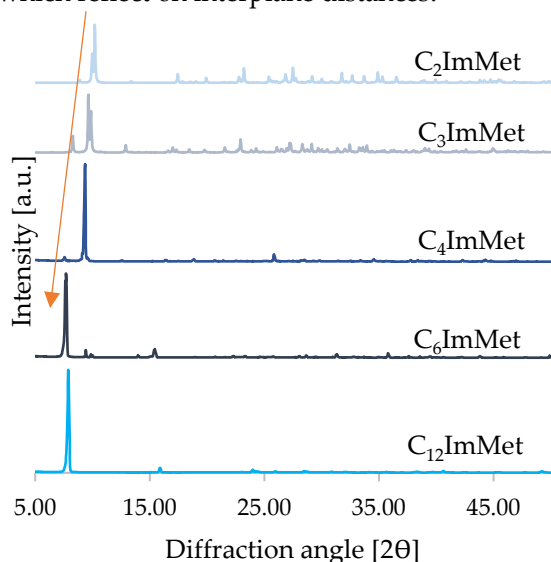


Fig. 8. Alkyl-methyl imidazolium lead iodide XRD spectra, with increasing alkyl length in direction of orange arrow

Thermogravimetric analysis of these perovskites confirmed their stability below 255°C.

Perfluoroalkyl-methyl imidazolium perovskites syntheses do not create crystals with enough quality to resolve single crystal structures. However, perovskite formation was confirmed by FTIR spectra showing the same change in imidazolium peaks described before. In this case PXRD diffractograms show a different pattern in respect to perovskites containing  $C_m\text{ImMet}$  cations, with a strong peak around 5.5° (Fig. 9). This suggests a different crystalline structure and confirms that the presence of fluorinated chains may have strong effects on perovskite structure.

Further analysis (solid state NMR or single crystals) is required to better understand the structural organization.

TGA shows onset of degradation at 200°C for  $C_5F_7\text{ImMet}$  and 256°C for  $C_9F_{13}\text{ImMet}$ , revealing the high stability of such materials.

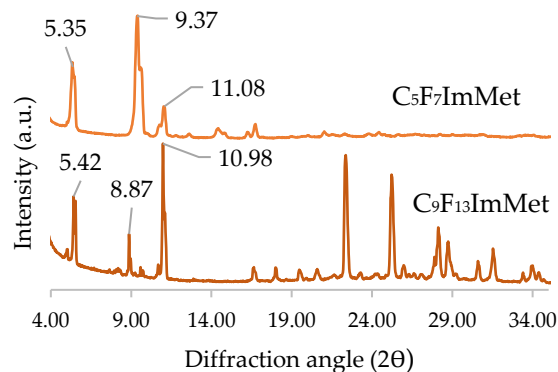


Fig. 9. Comparison among  $C_5F_7\text{ImMet}$  and  $C_9F_{13}\text{ImMet}$  lead iodides powder XRD spectra, with peaks in initial region

Hypothesis of ordered structures induced by perfluoroalkyl chains was evaluated through study of liquid crystal behavior with birefringence, through polarized optical microscope (POM). This effect was reported for  $C_9F_{13}\text{ImMetI}^-$  thanks to *fluorous-fluorous* interactions, and it was investigated for perovskite with this cation. [4] POM revealed that  $C_9F_{13}\text{ImMet}$  is an enantiotropic liquid crystal with Smectic A (SmA) phase. The Cr-SmA transition occurs at 144°C (Fig. 10), while it becomes an isotropic liquid at 236°C

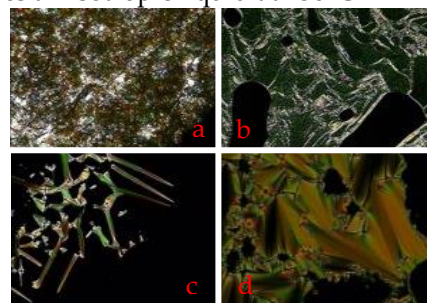


Fig. 10.  $C_9F_{13}\text{ImMet}$  phase transition observed at Polarized optical microscope: (a) solid at 25°C, SmA at 150°C (b) on heating and (d) on cooling and (c) clearing point at 236°C

Despite  $C_{12}\text{ImMetI}^-$  has a liquid crystal behavior with a smectic phase like  $C_9F_{13}\text{ImMet}$ , its perovskite does not exhibit this effect. Therefore, we can hypothesize that perfluoroalkyl chain are responsible for this behavior. Interaction among long perfluoroalkyl chains produces the segregation of fluorinated moieties, creating a lamellar order typical of smectic phase.

The hydrophobic effect of perfluoroalkyl chains was evaluated through contact angle (CA) measures for films deposited by drop casting of

Perovskite/DMF 1M solution on glass slides. Values after annealing at 90°C for 1 hour were compared to uncoated glass (control) and coated with imidazolium lead iodide (ImPbI<sub>3</sub>). C<sub>m</sub>ImMet lead iodides CA values increase with longer alkylated chains, as shown in Fig. 11 and Table 2. Hydrophobic behavior was obtained with alkyl chains longer than 6, as shown in Fig. 12. Concerning perfluoroalkyl chains, hydrophobic effect was obtained and enhanced with longer chains, as shown in Fig. 11 and Fig. 12d and e.

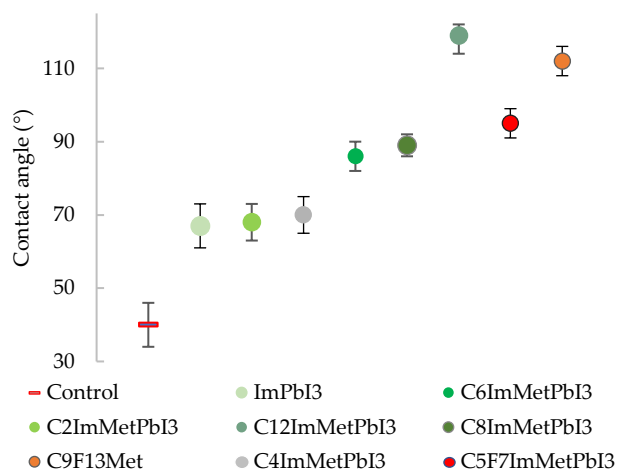


Fig. 11 Contact angle values after annealing for samples coated with perovskite with drop casting

Table 2. Contact angle after annealing

	CA post annealing
Control	40±6°
Im	67±6°
C <sub>2</sub> ImMet	68±5°
C <sub>4</sub> ImMet	70±4°
C <sub>6</sub> ImMet	88±2°
C <sub>8</sub> ImMet	89±3°
C <sub>12</sub> ImMet	119±9°
C <sub>5</sub> F <sub>7</sub> ImMet	95±4°
C <sub>9</sub> F <sub>13</sub> ImMet	112±4°

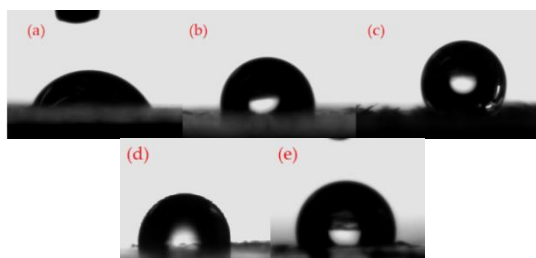


Fig. 12. (a) Imidazole, (b) C<sub>6</sub>ImMet, (c) C<sub>12</sub>ImMet, (d) C<sub>5</sub>F<sub>7</sub>ImMet and (e) C<sub>9</sub>F<sub>13</sub>ImMet lead iodide perovskite contact angle

Photophysical properties were first studied through UV-Vis spectroscopy: absorption spectra shown an initial transition with first peak caused from exciton formation in lead iodide chains, as shown in Fig. 13 [7]. Bandgap values were obtained between 2.28 eV and 2.6 eV.

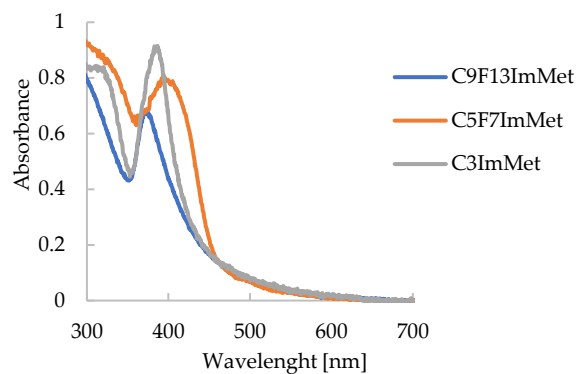


Fig. 13. UV-Vis spectra of C<sub>5</sub>F<sub>7</sub>ImMet (blue), C<sub>9</sub>F<sub>13</sub>ImMet (orange) and C<sub>3</sub>ImMet (grey) lead iodides

Photoluminescence (PL) of C<sub>m</sub>MetIm lead iodides is characterized by a Stoke-shifted broad band induced by self-trapped exciton emission related to 1D perovskite. As shown in Fig. 14, this band moves to lower wavelength and lower intensity increasing alkyl chain length. Similar to C<sub>m</sub>ImMet(PbBr<sub>3</sub>) this effect could be ascribed to different distortion of lead iodide sublattice, which influences self-trapped exciton. [5] However, these materials do not show a thermochromic effect as reported for lead bromide[5], but only an enhancement of intensity and longer relaxation time at lower temperatures, as expected for lead iodide perovskite. [7]

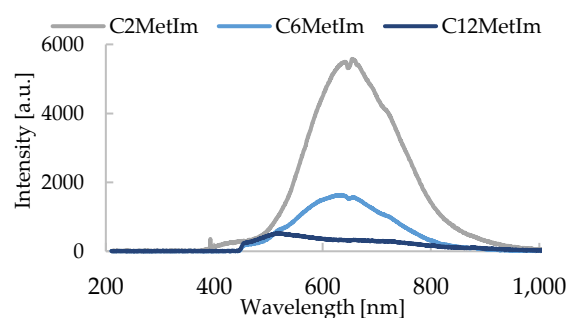


Fig. 14. PL emission for C<sub>2</sub>MetIm, C<sub>6</sub>MetIm and C<sub>12</sub>MetIm lead iodides with excitation at 355nm

As shown in Fig. 15, PL emission of perfluoroalkyl perovskites shows sharper peak in at lower wavelength (around 520 nm). This could suggest a different organization of lead iodide sublattice or more phases. Higher intensity has been measured

with the perovskite containing the  $C_9F_{13}ImMet$  cation with respect to  $C_5F_7ImMet$  and long alkyl chains and this would suggest a higher structural order as a consequence of segregation of longer perfluoroalkyl chains.

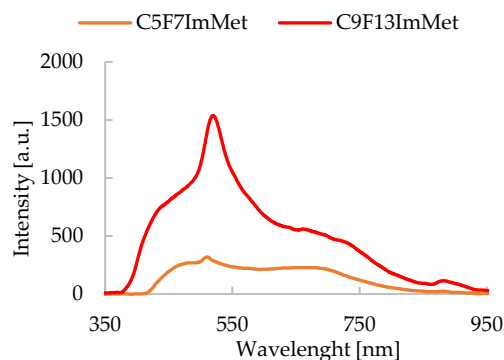


Fig. 15. PL emission for  $C_9F_{13}ImMet$  (red) and  $C_5F_7ImMet$  (orange) lead iodides with excitation at 355nm

### 3. Conclusions

In this work new lead iodide perovskites containing imidazolium cations decorated with alkyl or perfluoroalkyl chains of different length were synthesized and characterized. With alkyl-methyl imidazolium cations 1D HPs have been obtained, in good agreement with literature data, while in the presence of fluorinated cations, PXRD analysis suggests a different structure. Probably this is a consequence of the high tendency to segregation of fluorinated chains. In fact, for the perovskite containing  $C_9F_{13}ImMet$  for the first time a liquid crystalline behavior, with formation of a smectic phase has been observed.

PL emission, with sharper peaks than  $C_mImMet$  perovskites and higher intensity with respect to  $C_5F_7ImMet$  and long alkyl chains-imidazolium HPs, suggests ordered structures.

An additional effect made from perfluoroalkyl chains is the hydrophobic effect, interesting property in term of moisture resistance.

New perovskites with perfluoroalkyl chains with conjugated cations could be studied with the aim of using perfluoroalkyl chains as a new tool for their molecular design.

### 4. Materials synthesis

Imidazolium and its alkyl methyl salts were purchased from Sigma Aldrich, with exception of  $C_8ImMetI^-$  and perfluoroalkyl-substituted imidazolium. They were synthesized through reaction between 1-methylimidazole with 1-iodo-alkyl or perfluoroalkyl chain (molar ratio 1.1:1) in reflux of toluene for 48 hours.

Then compounds were washed with toluene and hexane to remove excess of reagents and dried under vacuum. Perovskites were synthesized through a reaction of lead iodide (1 eq.) and imidazolium salts (2 eq. as described from Seth.)<sup>[7]</sup> dissolved in a huge excess of aqueous solution of HI (57%wt) under  $N_2$  atmosphere at 110°C for 24 hours. Then yellow needle-shape crystals were obtained filtering in Bucker and washing with ethanol. In case of alkyl chains longer than 4 atoms, precipitation was obtained adding 1mL of ethanol and keeping solution in fridge for 1 night.

Hydrophobic behavior was evaluated with deposition of 1M Perovskite/DMF solution on glass treated with ozone. Contact angles were measured after annealing step at 90°C for 1 hour, made to remove residual DMF.

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