Templating Effect of Diammonium Cations on the Structural and Optical Properties of Lead Bromide Perovskites

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ABSTRACT

The role of templating the formation of 2D metal halide perovskites has been investigated by considering the 1,3-phenylenediammonium (1,3-PDA), 1,3-xylylenediamimonium (1,3-XDA), 1,4-phenylenediammonium (1,4-PDA), and 1,4-xylylenediamimonium (1,4-XDA) cations in lead bromide systems. Single-crystal x-ray diffraction confirms the formation 2D Dion-Jacobons (DJ) perovskites for all the cations except for the 1,3-XDA cation leading to a so-called 0D perovskitoid. Analysis of the structural data showed a higher distortion degree for the systems containing the shorter cation, namely 1,4-PDA. A detailed spectroscopic investigation, with both static and time resolved photoluminescence spectroscopy, revealed a broadband emissive component at room temperature with hundreds of nanometers of bandwidth when 1,3-PDA and 1,4-PDA cations are present, while a narrow peak is found for the longer cation, i.e. 1,4-XDA. A broadband emission arises in this last sample as well by decreasing temperature. Such broad emission, as indicated by the analysis of the power and temperature dependence of the PL, can be attributed to trap-mediated excitonic recombination or STEs, and the trend in emissive properties can be correlated to the different level of octahedral distortions. The novel systems reported in this work enlarge the family of broadband emitters and add further clues to develop efficient perovskite-based broadband and white light emitters.

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Introduction

In the last years there has been a growing interest around layered or two-dimensional (2D) metal halide perovskite (MHPs) for their superior stability and rich structural diversity, which may found application in several devices spanning from photovoltaics to lasing.[1,2] The most investigated families of 2D perovskites are the Ruddlesden-Popper (RP) and Dion-Jacobson (DJ) phases of general formula $A'_2A_{n-1}M_nX_{3n+1}$ and $A'A_{n-1}M_nX_{3n+1}$, respectively, where A′ and A are organic cations, and n represents the number of staggered inorganic layers made of metal M and halide X.[3] Most of the investigated organic spacers for 2D perovskites, to date, are monoammonium cations, while diammonium cations have been less explored.[3] In the latter case, and in particular for short cations, the DJ phases are generally formed, where the inorganic layers are stacked in an eclipsed fashion on top of each other, differently from RP where they are staggered.[3] In addition, not always a diammonium cation stabilizes a 2D perovskite, and 1D structures, characterized by linear chains of octahedra, have been also often observed. For example, in the series of linear cations of general formula $NH_3(CH_2)_mNH_3^{2+}$ (m = 4, 7, 8, 10, 12), the cations with even carbon-chain lengths formed 2D perovskites, while those with odd carbon chain lengths formed a 1D structure.[4] Very recently, the structural diversity of systems incorporating a diammonium cations has been further expanded towards 3D halide *perovskitoids* using linear cations such as 1,4-butanediamine (1,4BDA), N,N-dimethyl-1,3-propanediamine (NMPA), or N,Ndimethylethylenediamine (DMEA) providing a structural motif comprising dimers with edge-sharing octahedra which are then connected through corner-sharing bond to form a 3D network.[5] In these systems, the optical properties are close to traditional 3D MHPs with the bandgap being mainly influenced by standard octahedra distortion parameters. The correlation between structural distortions and optical properties in 2D perovskites is a key topic to modulate their properties and design novel and optimized materials. Thanks to the vast work performed on perovskites including monoammonium

cations, well-defined parameters have been defined and a careful materials design is now possible.[3] On the other hand, such kind of correlation is still partially missing on perovskites including a diammonium cations. In this context, the most relevant studies have been carried out on some limited compositions including, for example, 2,2′-(ethylenedioxy)bis(ethylammonium) (EDBE), N^1-methylethane-1,2-diammonium (*N*-MEDA), and 3-(2-ammonioethyl)anilinium (AEA) due to the interest in their very broad (white) emission.[6–9] In (EDBE)PbBr$_4$, the strong structural distortion induced by the organic spacer closely affects its defectivity leading to the formation of V_F centers whose radiative decay ultimately leads to broadened photoluminescence (PL).[6] In the other Pb-Br lead perovskites, where crystal structure was solved by x-ray diffraction (XRD) on single crystals, the broadband emission was as well correlated to self-trapping of photogenerated carriers through excited-state lattice distortions.[9] The work of Smith and co-workers put in prominence, among other structural parameters, the influence, on the relative intensity of the broad emission, of the distortion along the Pb-Br-Pb bond axis.[9] These results on diammonium cations further confirm, also for this type of ditopic ligands, the possibility of inducing slight distortions in the inorganic lattice by playing with the nature of the organic cation and therefore finely modulating the optical properties. However, the set of available structural data from single crystal diffraction – and their correlation with optical properties – on diammonium cations is still limited. In this work we enlarge the family of Pb-Br layered perovskites by a systematic and rationale investigation of the four diammonium cations represented in Figure 1 (the corresponding amines), namely 1,3-phenylenediammonium (1,3-PDA), 1,3-xylylenediamimonium (1,3-XDA), 1,4-phenylenediammonium (1,4-PDA), and 1,4-xylylenediamimonium (1,4-XDA).

1,3-phenylenediammonium (1,3-PDA)

1,3-xylylenediamimonium (1,3-XDA)

1,4-phenylenediammonium (1,4-PDA)

1,4-xylylenediamimonium (1,4-XDA)

Figure 1. Starting diamines used in the present paper for the synthesis of Pb-Br perovskites.

The first two spacers have been recently investigated in Pb-I and Pb-Br thin films highlighting their improved moisture resistance (in particular for 1,4-XDA). In absence of single crystal XRD data, it was concluded that the systems based on 1,4-PDA did not form a well-defined layered structure, due to the lack of flexibility of the PDA spacer, as well as its lower level of penetration into the neighboring perovskite layers, which prevents the formation of a layered phase.[10] Optical bandgap was reported to increase with the length of the alkyl chain but a clear correlation with optical properties was hindered by the lack of any structural data.[10] Concerning the 1,3-PDA and 1,3-XDA, the first cation has been investigated in Pb-I 2D perovskites as a function of the number of inorganic layers, n, (providing the crystal structure), showing the formation of DJ 2D perovskites and the expected increase of the bandgap by increasing n.[11] These two cations have not yet been investigated in Pb-Br perovskites and, in particular, 1,3-XDA-based lead halide systems have not reported in the current literature.

In the present paper, we synthesize lead bromide 2D perovskites (n=1) including the four diammonium cations mentioned above. We grew single crystals and we solved the crystal structures, and we report a detailed investigation of the optical properties, providing correlations with the bonding details and the interplay between the organic and inorganic components,

which is a crucial step for the understanding of structure-property relationships in monoammonium-based 2D perovskites.

Results and Discussion

A$_2$PbBr$_4$ 2D perovskites (A= 1,3-phenylenediammonium (1,3-PDA), 1,3-xylylenediamimonium (1,3-XDA), 1,4-phenylenediammonium (1,4-PDA), and 1,4-xylylenediamimonium (1,4-XDA), cfr. Figure 1) have been prepared by wet-chemistry route as reported in the Experimental Section. Single crystal XRD revealed that the compounds crystallize in triclinic and monoclinic space groups, as reported in Table 1.

Table 1: Crystal structure data for A$_2$PbBr$_4$ samples (A= 1,3-PDA, 1,3-XDA, 1,4-PDA, and 1,4-PDA).

Sample	Chemical formula	Space group and lattice volume (Å^3)	a, b, c (Å)	α, β, γ (°)
(1,3-PDA)PbBr$_4$	(1,3-C$_6$H$_{10}$N$_2$)PbBr$_4$	$C2/c$ Monoclinic 1357.8(8)	21.784(7) 8.821(3) 7.398(3)	90 107.214(9) 90
(1,3-XDA)$_2$PbBr$_6$	(1,3-C$_8$H$_{14}$N$_2$)$_2$PbBr$_6$	$P2_1/c$ Monoclinic 1299.4(4)	10.7571(18) 14.525(3) 8.5545(10)	90 103.540(4) 90
(1,4-PDA)PbBr$_4$	(1,. 4-C$_6$H$_{10}$N$_2$)PbBr$_4$	P-1 Triclinic 658.9(4)	7.434(3) 8.712(3) 11.028(4)	70.570(19) 78.527(19) 89.414(19)
(1,4-XDA)PbBr$_4$	(1,4-C$_8$H$_{14}$N$_2$) PbBr$_4$	$P2_1/c$ Monoclinic 821.68(7)	12.3274(7) 8.1618(4) 8.1675(4)	90 90.817(2) 90

Not all the samples investigated crystallize as a layered perovskite structure, in particular this does not occur for the composition including the 1,3-XDA cation, giving the chemical formula (1,3-XDA)$_2$PbBr$_6$. A sketch of the crystal structures is reported in Figure 2.

Figure 2: Crystal structures of a) (1,3-PDA)PbBr$_4$, b) (1,3-XDA)$_2$PbBr$_6$, c) (1,4-PDA)PbBr$_4$, d) (1,4-XDA)PbBr$_4$.

As mentioned, (1,3-XDA)$_2$PbBr$_6$ does not assume the perovskite structure, being constituted by slightly distorted isolated octahedra, corresponding to a so-called 0D perovskitoid. The crystal cohesion is then given by the aromatic cations whose NH$_3^+$ groups interact with both equatorial and axial Br atoms. To the best of our knowledge, this is one of the first 0D bromide perovskite derivative including a diammonium cation, while chloride containing 0D systems have been reported in the past.[12] (1,3-PDA)PbBr$_4$, (1,4-PDA)PbBr$_4$, and (1,4-XDA)PbBr$_4$ occur as DJ phases with n=1, according to the general formula A'A$_{n-1}$M$_n$X$_{3n+1}$. They all comprise layers of PbBr$_6$ octahedra separated by layers of organic cations. The aromatic cations interact with the inorganic framework in the terminal mode. The interaction between the NH$_3^+$ terminal group and the inorganic framework is known to affect the structure and properties of hybrid halide perovskites.[13,14] In the case of diammonium cations, it was

already reported that some cations cannot give layered perovskite structures. For example, even-membered alkyl chains with ammonium groups at both ends form layered perovskite-type hybrid structures, both in bromide and iodide compounds whereas odd-membered chains do not[15]. The layered perovskite structure is adopted only when the chains are kinked so that the hydrogens on both ends of the organic molecules can hydrogen bond to the halides of the inorganic layers[15]. Moving away from linear chains, it has been shown that cations with fused aromatic rings can give the layered perovskite structure only when the cation is able to tilt and hydrogen bond to the halides[15]. More generally, aromatic cations where the ammonium groups may have no degree of freedom, does not necessarily give the layered perovskite motif and 1D motifs are observed for 4,4′-MDAPbI$_4$[15] [MDA=methylenedianilinium ($H_3NC_6H_4CH_2C_6H_4NH_3$)], (1,4PDA)PbI4[16], whereas the aforementioned (1,3-PDA)PbBr$_4$, (1,4-PDA)PbBr$_4$, (1,4-XDA)PbBr$_4$, together with (1,3-PDA)PbI$_4$[17], (1,3-PDA)PbCl$_4$[12] and (AEA)PbBr$_4$ form a layered perovskite structure.[18] The XRD powder patterns obtained on the crushed crystals are reported in Figure 3 superimposed to the calculated patterns from the single crystal XRD data.

Figure 3: XRD powder patterns of a) (1,3-PDA)PbBr$_4$, b) (1,3-XDA)$_2$PbBr$_6$, c) (1,4-PDA)PbBr$_4$, d) (1,4-XDA)PbBr$_4$ superimposed to the calculated pattern from SC-XRD (vertical red bars).

We can further explore the interaction between the inorganic framework and the organic cation using the penetration depth, defined as the distance between the N atom of the amino group and the plane of the terminal halides[14]. The NH$_3^+$ penetration affects both the distortion between the octahedra, in term of deviation from 180° of the Pb-X-Pb angle, and within the octahedra, in terms of octahedral elongation length ($\langle \lambda_{oct} \rangle$) and their bond angle variance (σ_{oct}^2), as defined by Robison et al. (1971)[19]. By comparing the present data for the 2D perovskites, and the above mentioned reported systems including diammonium cations, it is possible to note that the Pb-X-Pb angle increases with increasing penetration with a linear trend from chloride to iodide (Figure S1).[14] It is worth noting that (1,4-PDA)PbBr$_4$ falls outside this trend, probably because the PDA cation is short and rigid, and because of the increasing strength of the hydrogen bond from I to Br to Cl.[20,21] For the present 2D DJ perovskites, the values of the average Pb-Br-Pb angles are 142.95° for (1,3-PDA)PbBr$_4$, 142.12° for (1,4-PDA)PbBr$_4$, and 150.21° for (1,4-XDA)PbBr$_4$, indicating therefore a greater distortion for the two short diammonium cations with respect to 1,4-XDA. The plots correlating the octahedral elongation

and bond angle variance of present 2D perovskites, and other DJ systems based on diammonium cations where crystal structure data are available, are reported in Figures 4a and 4b.

Figure 4: a) Octahedral elongation, and b) bond angle variance as a function of NH_3 penetration. PDA= phenylenediammonium; AEA=3-(2-ammonioethyl)anilinium; XDA= xylylenediamimonium; AMC=1,4-bis(ammoniomethyl)cyclohexane

It is clear that the octahedral elongation and bond angle variance of this group of compounds decrease as the NH_3^+ penetration increases. This effect may be a consequence of the flexibility of the organic cation. In fact, the 1,3-PDA cation, where all the atoms except the hydrogens are forced to lie in the same plane, induce the larger distortion among all the

investigated halides[12,22]. Notably, the 1,4-PDA cation induces a distortion within the octahedra similar to the 1,3-PDA cation, whilst the distortion decreases for the 1,4-XDA that is more flexible since the nitrogen atoms are not bound to stay in the same plane as the aromatic ring. The smallest distortion is shown by 1,4-AMC cation, which is the aliphatic analogue of 1,4-XDA, suggesting a conjugate ring provide more rigid structural constranits.[17]

This reasoning is further confirmed by the room temperature Raman spectra for (1,3-PDA)PbBr$_4$, (1,4-PDA)PbBr$_4$, and (1,4-XDA)PbBr$_4$ samples reported in Figure 5 in the range 70-250 cm^{-1}.

Figure 5: Room temperature Raman spectra of 1,3-PDA (blue line), 1,4-PDA (green line and 1,4-XDA (red line) excited at 632.8 nm with microscopic resolution. All the spectra are the average over 10 spectra collected along a line of 30 μm.

According to ref. 23 in this energy region two main vibrating reservoirs should be active: the stretching and bending modes of the Pb-Br cages in the lower energy part and the libration of the organic cations partially bound to the Pb-Br framework.[23] At first, we observe for all the investigated samples well defined Raman fingerprints thus confirming a high crystal quality. In addition the data pointed out that the Raman yields from (1,3-PDA)PbBr$_4$, (1,4-PDA)PbBr$_4$ are

markedly lower with respect to that from (1,4-XDA)PbBr$_4$. This is particularly clear for the mode observed for 1,4-XDA at 78.5 cm^{-1} probably associated to the stretching motion of Pb-Br unit. For (1,3-PDA)PbBr$_4$, (1,4-PDA)PbBr$_4$ weaker bands are observed at 88 cm^{-1}. This behaviour is consistent with the greater distortion affecting the two short diammonium cations with respect to 1,4-XDA. In the region 130-250 cm^{-1} we observe, in comparison with the octahedral Raman yield, a small Raman activity decrease for 1,4-PDA and 1,4-XDA with respect to 1,3-PDA. Even if a detailed mode attribution is required this could be due to the smaller NH$_3^+$ penetration characterizing 1,3-PDA sample.

The importance of the flexibility of the organic cation is confirmed by a closer analysis of the octahedral distortion reported in Figure 6. In this plot, related to the octahedra structural parameters, we could also include those perovskite derivatives not crystallizing as 2D systems. For these systems, the distortion is mostly due to the arrangement of the inorganic framework. In particular, in (1,4-PDA)PbI$_4$ the asymmetric unit contains a Pb atom on a site of 2/m symmetry and two I atoms on mirror planes and thus, by symmetry, the equatorial plane is defined by four equivalent positions for atom I2, whereas the two equivalent positions for atom I1 are necessarily axial.[16] The symmetry constrains together with the edge sharing motif that occurs through the equatorial I atoms give rise to regular octahedra. (1,3-XDA)$_2$PbBr$_6$ comprises isolated and slightly distorted octahedra, characterized by a relatively high angle variance, suggesting a deviation of the Br-Pb-Br angles from 90°. The crystal cohesion is given by a framework of contacts between the amino groups and the bromide atoms. The organic molecule present in the asymmetric unit is tilted of 20° with respect to (001) plane. Coming to the layered perovskites, the octahedra show large distortion when cations where the nitrogen atoms are bound to sit in the same plane as the aromatic cation, such as the 1,3-PDA and 1,4-PDA, are present. On the other hand, the more flexible 1,4-XDA cation induces only a slight distortion in the PbBr$_6$ octahedra. Analogously with the AEA cation, where one nitrogen atom is bound to aromatic plane and the other one is not, the octahedra adopt a distortion between

the ones reported for 1,4-XDA and 1,4-PDA.[18] Again, based on the present results, the 2D DJ

perovskites reported in this work show an octahedral distortion increasing passing from (1,4-

XDA)$PbBr_4$ to (1,4-PDA)$PbBr_4$ and to (1,3-PDA)$PbBr_4$, with the last two showing, in particular,

a significant increase in the octahedral angle variance with respect to (1,4-XDA)$PbBr_4$.

Figure 6: Distortion parameters for the newly synthesized compounds and already reported materials with similar characteristics. Open symbols mark compositions that do not crystallize in a layered perovskite structure.

To further investigate the relationship between the structure of the perovskites, in

particular the degree of octahedra distortion, and their optical properties, we performed an in-

depth spectroscopic study on the samples which present the 2D DJ structure: (1,3-PDA)$PbBr_4$,

(1,4-PDA)$PbBr_4$, and (1,4-XDA)$PbBr_4$.

The materials' static absorbance and photoluminescence (PL) at room temperature are presented in Figure 7a. For all samples the absorbance (dashed lines), calculated from the reflectivity of powdered single crystals, shows an absorption edge well close to the UV range (between 380 nm and 420 nm) as expected for two – dimensional Pb bromides.[24–26] Furthermore, even at room temperature a relatively narrow absorption peak can be observed on top of the band edge, consistent with stable excitonic population, typical of quantum confinement effect.[25]

Figure 7: a) Absorption (dashed lines) and PL (slid lines) spectra of 1,3-PDA (blue line), 1,4-PDA (gree line and 1,4-XDA (red line) at 297K. b)-d) Temperature-dependent photoluminescence spectra of: b) (1,3PDA)PbBr$_4$, c) (1.4 PDA)PbBr$_4$, d) (1,4 XDA)PbBr$_4$. All spectra are acquired using an excitation wavelength, λ_{ex}, at 355nm between 77 and 297K.

The static PL (solid lines) measured under pulsed excitation at 355 nm shows a more diverse picture: only 1,4-XDA shows a narrow peak (≈26 nm bandwidth) centered at 421 nm with a Stokes shift of only a few nm, as expected from excitonic photoluminescence. On the other hand, 1,3-PDA and 1,4-PDA show very broad emission peaks centered respectively at

650 nm and at 565 nm, with FWHMs of hundreds of nm. Such bright and broadband emission is typical of highly distorted 2D materials, where excitonic recombination is mediated by defects or self-trapping resulting in a significant red shift and broadening of the PL peak.[7,24]

To better understand the nature of the photoluminescence we measured temperature dependent PL spectra between 77 and 297 K (Figure 7b-d). The two samples with a higher (and similar) degree of distortion, 1,3-PDA and 1,4-PDA, show a similar trend, with a bright and broad feature dominating the emission at all considered temperatures; intriguingly a small narrow feature appears at 420 nm for 1,3-PDA while cooling down. At lower temperatures 1,4-PDA luminescence efficiency is boosted (Figure S2). In 1,4-XDA the PL is still dominated by the narrowband emission at 420 nm, with broadband emission centered at around 575 nm arising as the temperature decreases.

Significant insight into the relationship between light emission and structural parameters can be gleaned from a more careful analysis of the temperature dependence of the PL. First of all, we analyze the temperature dependence of the integrated PL intensity (Figure 8a), integrating the broadband emission, *i.e*. the broad emission of 1,3-PDA (500 – 850 nm) and 1,4 –PDA (550 – 700 nm), and 1,4-XDA (500 – 950 nm). For all three materials, the PL intensity decreases going from 77 K to room temperature, suggesting the presence of thermally activated non radiative recombination channels which compete with radiative excitonic recombination. For all three materials we fit the data with an Arrhenius curve to estimate the activation energy for non-radiative recombination pathways. The obtained activation energies are $\Delta E_{1,4\text{-PDA}}$=95meV, $\Delta E_{1,3\text{-PDA}}$=39meV and $\Delta E_{1,4\text{-XDA}}$=71meV. We note that in the case of 1,4-XDA, the recombination channel might be back transfer to the excitonic state, which indeed is the brightest emissive feature for this material. A higher value of ΔE is desirable for photoluminescence application, indicating a PL more stable at room temperature. Indeed, 1,4-PDA shows a large ΔE and consistently shows a very promising intense luminescence.[27]

We then consider the variation of the luminescence bandwidth, estimated by fitting the main emission component (at 650 nm and 550 nm for 1,3-PDA and 1,4-PDA respectively and at 420 nm for 1,4-XDA) with a Gaussian and taking its FWHM (Figure 8b). The broad luminescence of 1,4-XDA is not considered in this analysis as its superimposition to the narrow component makes it hard to isolate correctly, especially at higher temperatures.

The PL FWHM can be used to evaluate the coupling of the carriers – excitons in this case - with phonons by fitting the FWHM trend vs. temperature with equation (1), thus obtaining the Huang-Rhys factor and the energy of the involved phonons.[28–30]

$$FWHM(T) = 2.36\sqrt{S}E_{ph}\sqrt{\coth\frac{E_{ph}}{2k_BT}} \tag{1}$$

Here S is the Huang-Rhys factor and E_{ph} is the phonons energy. A large value of S is related to significant degree of carrier – phonon coupling, indicative of either emission by STEs or phonon mediated detrapping and radiative recombination. Indeed, for the two samples with broadband emission, 1,3-PDA and 1,4-PDA, we obtain respectively S=39.09 and S=131.6. For the excitonic component of 1,4-XDA on the other hand we obtain and S=8.58 with E_{ph}=12.12 meV. Values of S >10 have been associated with the presence of STEs in perovskites and organic materials: in the broadband emitters, the coupling between phonons and carriers is compatible with the formation of self-trapped exciton which can explain the broad emission from these samples.[30–32] In particular, the bright 1,4-PDA has the largest Huang-Rhys factor, indicating very efficient coupling with phonons with E = 13 meV. On the contrary, the value of S extrapolated for the last sample (1,4-XDA) is small, which agrees with an emission due to recombination of free excitons.

Figure 8: a) Integrated PL intensity and b) FWHM as function of temperature, measured under pulsed excitation (1 kHz) at λ_{ex} =355 nm. c) Fluence dependence of the integrated PL intensity at 77 K fitted with a power law d) Time - resolved photoluminescence within an integration range of 400-450 nm (dashed line, under 80 MHz pulsed excitation) and 500-900nm (continuous line, 1 kHz).

Further indication on the nature of the broad emission comes from the pump fluence dependence of PL (Figure S3). Fitting the intensity of emission in function of the incident power with a power law $I=P^K$ we estimate exponential K (Figure 8c): the values $K_{1,3\text{-PDA}}$=0.745 and $K_{1,4\text{-PDA}}$=0.835, lower than 1, indicate a recombination pathway mediated by defects leading to the formation of self-trapped excitons.[8,24,33] A purely excitonic recombination on the other hand is expected to yield a power dependence with K = 1. However, it is no possible to compare this power law with the narrow emission of 1,4-XDA: its small Stokes shift results in significant reabsorption in powdered single crystal samples, distorting the measured spectrum. Furthermore, while 1,3-PDA and 1,4-PDA have remarkably photostable emissions, 1,4-XDA is unstable under prolonged intense illumination, even on a scale of a few seconds (Figure S4). With the excitonic component decreasing faster than the broad emission, making a fluence dependence measurement unreliable.

To validate the idea of different origins for the emission of the samples, we performed time resolved photoluminescence measurement at 77 K in different time ranges (ps and ns) as shown in Figure 8d and Figure S5. In sample 1,4-XDA, the difference between the excitonic and broad emission is stark: while the excitonic component at 410 nm decays in $\tau = 76 +/- 2$ ps, in line with the expected excitonic lifetimes at 77 K, the broad emission has a decay 3 order of magnitude slower ($\tau = 180$ ns) which is compatible with a trap or phonon mediated process, with a consequent redshift of the PL emission.

Sample 1,3-PDA also shows a long-lived lifetime for its broad emission at 650 nm ($\tau = 8.5$ ns). Interestingly, in the high-resolution time-resolved measurement we also observe a narrowband component centered at 420 nm (FWHM = 20 nm), which has a very low intensity in the static PL measurements. This is related to its extremely short lifetime, which is shorter than the instruments response function indicating $\tau < 3.5$ ns: such rapid PL decay, coupled with the very low total intensity of this narrow band emission, points to emission from free exciton recombination that is swiftly quenched by transfer to states with red-shifted emission. Both the lifetime of narrow and broad emission of 1,3-PDA are almost an order of magnitude faster than the one of the sample 1,4-XDA: this is an indication, supported also by the brighter emission and higher activation energy for non-radiative pathways of the latter, that fast non-radiative recombination is the dominant mechanism in 1,3-PDA.

Lastly the sample 1,4-PDA, as in the static measures, shows only a broadband emission which presents a decay characterized by a late rise in the intensity (about 1000 ns) followed by a long decay over tens of µs. This could be an indication of a complete and efficient energy transfer from the higher energy free exciton to a red-shifted self-trapped exciton with an efficient radiative recombination mechanism. Consistently this sample has the highest ΔE ($\Delta E_{1,4-PDA}=95meV$) between the analyzed samples leading to a photoluminescence dominated by radiative recombination of carriers both at room and cryogenic temperature. The late rise in PL intensity suggests a back transfer mechanism from the non-radiative recombination sites to

the radiative one; this feature is not present in 1,3-PDA decay which emission is, in fact, dominated by non-radiative pathways, from which a back transfer to the radiative state is hindered.

As we have shown with both static and time resolved photoluminescence spectroscopy at 77 K, the three materials which form 2D Dion – Jacobson phases all exhibit a broadband emissive component with hundreds of nanometers of bandwidth. Such broad emission, as indicated by the analysis of the power and temperature dependence of the PL, can be attributed to trap-mediated excitonic recombination or STEs. In the case of 1,4-XDA, the strongest emission is not the broad band component, but rather a narrowband, short-lived component characterized by a small Stokes shift, which is consistent with the radiative recombination of free excitons; at room temperature this narrow band feature at 420 nm is the only significant emission.

The different luminescence of the three samples can be rationalized by considering their structural characteristics. The two materials, 1,3-PDA and 1,4-PDA, with larger values of σ^2 and λ_{oct} (Figure 6), show a dominant role of the broadband emission, as expected in materials with significant deviations from ideal octahedral geometry.[7] On the other hand, 1,4-XDA, which has relatively undistorted octahedra, but shows significant tilting of the Pb-Br-Pb angle ($< 150°$) exhibits a mixture of narrow and broad band emission, with only the free exciton component persisting at room temperature.[8] However, it is interesting to note that the respective degrees of inter- and intra-octahedral distortion are not sufficient to fully explain the luminescence properties we have observed. In particular, 1,3-PDA has a highly distorted geometry, very similar to 1,4-PDA in terms of the most commonly used short-hands for octahedral distortion: their values of λ_{oct}, σ^2 and D_{tilt} are comparable. However, 1,3-PDA also shows a small narrowband component at 420 nm, which is quickly transferred (< 3 ps) to the broadband feature, but not before radiative free exciton recombination can occur. No such

feature is observed for 1,4-PDA: this behavior may indicate a much more effective transfer to the broadband emissive states which completely overtakes radiative recombination.

It should also be noted that 1,3-PDA is significantly less emissive that its 1,4 counterpart, pointing to a larger contribution from traps acting as non-radiative recombination centers.

Conclusions

In this study we extended the family of DJ halide perovskite containing diammonium cations, by preparing, solving the structure, and characterizing novel lead bromide materials containing 1,3-phenylenediammonium (1,3-PDA), 1,3-xylylenediamimonium (1,3-XDA), 1,4-phenylenediammonium (1,4-PDA), and 1,4-xylylenediamimonium (1,4-XDA) cations. We showed that the choice of the organic cation has great influence on the topology of the structure, determining whether the layered perovskite structure can occur or not. Consistently, the degree of freedom of the organic cation deeply affects the interactions with the inorganic framework, influencing octahedral distortions and thus the optical properties of the compounds. Thanks to detailed structural and optical characterizations, we could link the differences in the optical properties, such as the nature of luminescence, to the structural parameters. In fact, samples with high degree of distortion (containing the 1,3-PDA and 1,4-PDA cations), *i.e.* with larger values of σ^2 and λ_{oct}, show a dominant role of the broadband emission, while the presence of relatively undistorted octahedra when 1,4-XDA cation is the spacer, leads to a mixture of narrow and broadband emission. However, the difference in optical properties, and in particular in the intensity of the emission, cannot be completely explained based on common and traditionally used parameters of the distortion in the octahedral layers. This suggests that further investigation into the relationship between structural properties and broadband luminescence in low-dimensional perovskites containing diammonium cations are called for to identify precise design rules allowing to develop efficient perovskite-based broadband and white light emitters.

Declaration of interests

The authors declare no competing interests.

Supplemental Information

Supporting Information Available: Materials and Methods, additional figures of photoluminescence measurements and distortion parameters.

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