

Two-Dimensional Perovskite Activation with an Organic Luminophore

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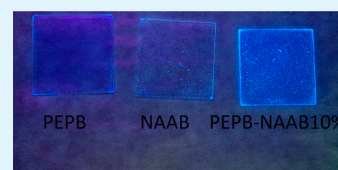
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S Supporting Information

ABSTRACT: A great advantage of the hybrid organic–inorganic perovskites is the chemical flexibility and the possibility of a molecular engineering of each part of the material (the inorganic part and the organic part respectively) in order to improve or add some functionalities. An adequately chosen organic luminophore has been introduced inside a lead bromide type organic–inorganic perovskite, while respecting the two-dimensional perovskite structure. A substantial increase of the brilliance of the perovskite is obtained. This activation of the perovskite luminescence by the adequate engineering of the organic part is an original approach, and is particularly interesting in the framework of the light-emitting devices such as organic light-emitting diodes (OLEDs) or lasers.

KEYWORDS: electronic materials, hybrid perovskites, chemical synthesis, photoluminescence activation, energy transfer, bidimensional structure, organic–inorganic semiconductor, excitons



INTRODUCTION

During the past 30 years, two-dimensional (2-D) organic–inorganic hybrid semiconductors have been paid substantial attention owing to their favorable properties and great application potential in optodevices.^{1–18} More recently, three-dimensional (3-D) perovskites have known an extraordinary resurgence of interest because of their performances in photovoltaic “dry Graetzel type” solar cells.^{19–25} However, the chemical flexibility of the 3-D perovskites is quite low, because of the high restrictions linked to their almost compact cubic lattices: the cation and anion dimensions should satisfy the relation $(R_A + R_X) = \sqrt{2}t(R_M + R_X)$, with t being an adjustment parameter which needs to be close to 1,^{26–29} so this leaves little choice for the cations besides cesium, ammonium, and methylammonium.

On the other hand, the 2-D perovskites are organic–inorganic crystals responding to the different $(R-NH_3)_2MX_4$ stoichiometry, where R is an organic group, and are self-assembled compounds forming well-ordered multilayered structures spontaneously. Each layer is also compact and this situation more or less imposes conditions on the bulkiness of the ammonium salt in the two dimensions of the plane;^{27,30} however, there is much more tolerance in the third dimension, because the plane stacking is much more flexible. This characteristic, inherent to the bidimensional organiza-

tion, introduces much flexibility with respect to the type of organic moiety which can be introduced in a 2-D perovskite, while retaining the special 2-D plane arrangements. The phenylethyl moiety is frequently the preferred choice to obtain a good quality 2-D arrangement, for reasons still not completely elucidated. However, we and others have shown that different other organic groups, such as methyladamantanyl or methyl- α -terthienyl, did lead to the 2-D perovskite structure.^{27,31,32}

While to date this chemical flexibility has mainly been used to introduce alkyl, heterocyclic, or fluorophenyl groups,^{32–35} mainly aiming at improving the perovskite stability, it is nevertheless a huge challenge to introduce functional groups to improve the performances of the materials. This improvement has already been envisaged and attempted first by Mitzi, who prepared lead chloride³⁶ and lead iodide³⁷ quaterthienylmethylammonium perovskites. However, his results and conclusions were that, in the case of the lead chloride perovskites, the luminescence was strictly due to the quaterthiophene (the perovskite acting only as an organizing host) although efficient hole and electron conduction could be achieved in these systems as compared to performances of the pure organic light-

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emitting diodes (OLEDs) at the time. In the case of the iodide-based perovskite, incorporating the same organic fluorophore,³⁷ an electron transfer occurred, oxidizing the iodide anion which almost completely quenched the emission. Other efforts have been made by Era,^{38,39} Ema,⁴⁰ and Morimoto⁴¹ with naphthalene chromophore, by Era^{39,42,43} with azobenzene, by Braun with pyrene chromophore,⁴⁴ by Hua with polyacetylenes,⁴⁵ by Li with *N*-(3-aminopropyl)imidazole,⁴⁶ and by Papavassiliou^{47,48} with naphthylmethylammonium, but in each case energy transfer occurs from the inorganic excitonic bands of the perovskite to the states of the chromophore linked ammonium molecules, increasing the emission of the chromophores. Additional works have been done to incorporate a blue fluorescent dye in a lead chloride based perovskite showing excited state intramolecular proton transfer reaction,⁴⁹ or to incorporate hole-transporting carbazole chromophore in an organic layer in order to modify the conduction properties.^{50,51} Finally, Kawano⁵² suggested that a resonance can be operative between the Frenkel and Wannier excitons in particular cases of naphthylmethylammonium containing $\text{PbBr}_x\text{I}_{4-x}$ perovskites. Therefore, up to now, cooperation between an organic fluorophore and a perovskite showing the activation of the perovskite luminescence has not been achieved.

Indeed, whatever the application considered, and like most inorganic materials (e.g., Q-dots),⁵³ the Achilles heel of perovskites is their very low absorption coefficient. We estimated it around $50 \text{ mol}^{-1} \text{ cm}^{-1}$, the molar concentration being defined with respect to a monomer unit containing one lead atom in the 2-D polymeric crystal. Therefore, among the most desired functional groups stand fluorophores able to act as “collecting antennas” for light, and transfer the energy to the emissive perovskite. Introducing an adequate light collector in the perovskite structure is therefore a serious goal and challenge since most organic dyes have their absorption coefficient in the range 10^4 – $10^5 \text{ mol}^{-1} \text{ cm}^{-1}$. Therefore, introducing an efficient “antenna” while retaining the perovskite structure might ideally improve the absorption coefficient and the brilliance of the material up to 1000 times if the energy transfer is efficient. Charge generation in a photovoltaic device might also be seriously improved. However, besides the appropriate steric hindrance, the fluorophores also need to fulfill two drastic additional conditions. First, they need to enable the energy transfer to the perovskite (relating to spectra matching), and second, the photoinduced electron transfer (PET) should be unfavorable. This is a serious point of concern, since both the metal (lead) and the halides that constitute the perovskite are redox-active.

In the present study, we describe activation of a lead bromide based perovskite using a 2,3-naphthalimide-ethylammonium partner, hereafter named NAAB (Figure 1). While the pure ammonium salt does not lead to the 2-D perovskite formation, we show that when it is diluted into a classical phenylethylammonium salt, a perovskite is indeed formed, which includes the fluorophore molecules. The material features an

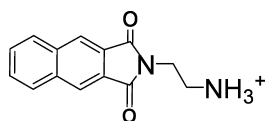


Figure 1. 2,3-Naphthalimide-ethylammonium molecule, called NAAB.

improved brilliance at a dilution around 10% of the fluorophores in the lattice.

EXPERIMENTAL SECTION

UV–vis absorption spectra of perovskite films were measured by a conventional PerkinElmer 950 UV/vis spectrometer; diffusion measurements could be additionally performed using a 100 mm integrating sphere. Photoluminescence spectra and excitation spectra were performed on a Fluorolog FL3-221 spectrofluorometer from Horiba Jobin-Yvon.

Synthesis of Ammonium Salts. Synthesis of Fluorophore Containing Ammonium Salt NAAB. Mono-NH-Boc-ethylenediamine (Aldrich 2.5 g, 11.7 mmol) was mixed with 2,3-naphthalene dicarboxylic anhydride (3.09 g, 11.7 mmol) in 50 mL of ethanol to reflux for 1 h. The precipitate was filtered and recrystallized in ethanol. The product, *N*-(2-ethyl-NH-Boc)-2,3-naphthalimide was dried under vacuum.

The fluorophore containing ammonium salt was synthesized following this procedure: a concentrated (~40%) HBr aqueous solution (in slight excess) was reacted with *N*-(2-ethyl-NH-Boc)-2,3-naphthalimide in diethyl ether (100 mL) under stirring at ambient temperature. Cleavage of the Boc group and salification occurred simultaneously and the corresponding white ammonium bromide, called NAAB, was obtained. NMR measurement was performed to verify the structure and the purity of the NAAB (see Supporting Information, Figures S1 and S2).

Synthesis of Phenylethylammonium Salt PEB. The phenylethylammonium bromide, called PEB, was prepared by reaction in stoichiometric equivalents of phenylethylamine (Sigma-Aldrich, ≥99%) with hydrobromic acid HBr (40%) in 100 mL of diethyl ether. The precipitate ammonium salt was filtered, dried in a vacuum, and put in a desiccator over phosphoric anhydride (P_2O_5) for several days before use.

Synthesis of Perovskite Layers. The prepared phenylethylammonium bromide (PEB) was mixed with lead bromide (PbBr_2) with a stoichiometry of 2:1 and dissolved in dimethylformamide (DMF) with a 1:10 mass ratio. With this solution, several perovskite precursor solutions were prepared by replacing, with proportions of 0, 10, and 20 mol %, the PEB ammonium salt by the NAAB salt: the perovskites prepared from these precursor solutions will be called respectively PEPB, PEPB-NAAB10%, and PEPB-NAAB20%. In particular, note that the precursor solution contained 0% NAAB, so containing only PEB will lead to the formation of the standard [bi-(phenylethylammonium)tetrabromoplumbate perovskite, called PEPB.^{27,35,54} These three solutions were dispersed on a quartz substrate by spin-coating at 2000 rpm for 30 s, and annealed at 60 °C under nitrogen in an oven. We obtained homogeneous organic–inorganic perovskite layers, presenting the same thickness: 50 nm (checked with atomic force microscopy (AFM) measurements as in refs 27, 35, and 54), for all the perovskite samples.

Additionally, a solution of pure NAAB in DMF was prepared in order to characterize the fluorophore ammonium salt itself (in the form of microcrystals). A cast film of the NAAB monomer microcrystals was performed on a quartz substrate; its thickness is 30 nm. The sample will be called NAAB in the following.

RESULTS AND DISCUSSION

Figure 2 exhibits the X-ray diffraction spectra of the three samples. For PEPB and PEPB-NAAB10%, numerous diffraction orders are present proving the high crystallinity of these thin layers.⁵⁵ On the contrary, it can be seen that fewer diffraction orders are present for the PEPB-NAAB20% sample, indicating a degraded crystallinity of the material. It can be concluded that incorporation of 20% of the NAAB salt already disrupts the organization of the perovskite. In a proportion above 20% in dilution with PEPB, no perovskite structure is obtained (absence of the classical perovskite features in X-ray diffraction spectra). Note that the same observation has been reported as

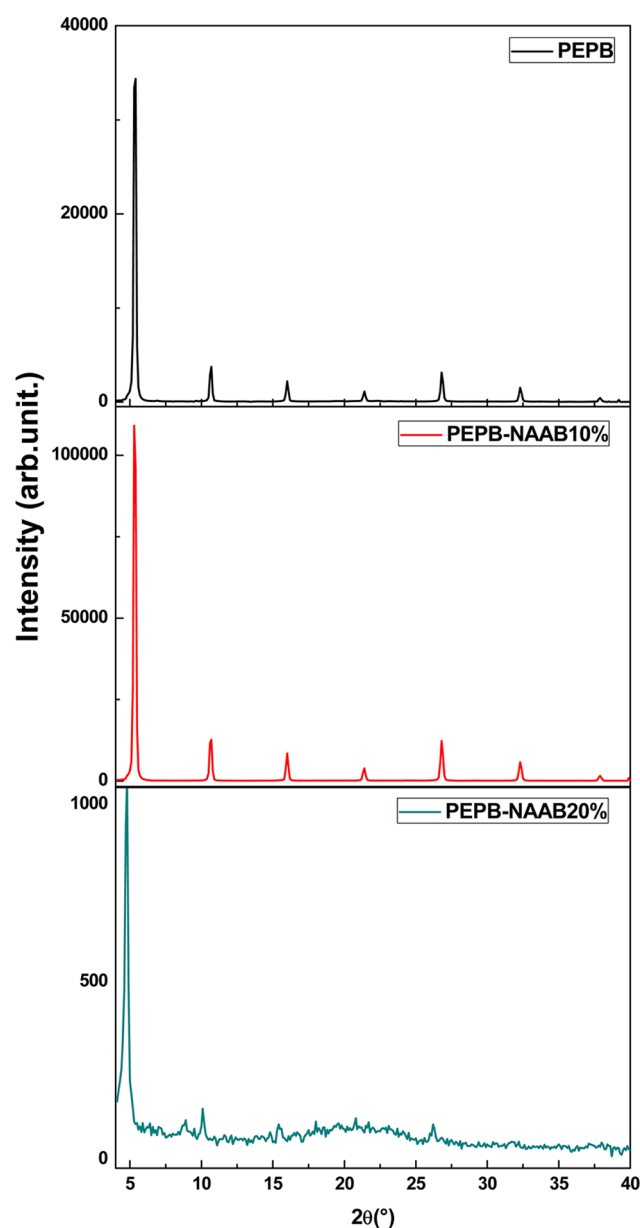


Figure 2. X-ray diffraction spectra of three perovskite layers: PEPB, PEPB-NAAB10%, and PEPB-NAAB20%.

well several years ago by Era in perovskites prepared by molecular mixing of carbazole-linked ammonium molecules and alkyl ammonium molecules in the organic layer.⁵⁶ As a consequence, in the following, we will focus our attention on the optical properties of PEPB-NAAB10%.

Figure 3 shows the absorption spectra of the three 50 nm thick PEPB, PEPB-NAAB10%, and PEPB-NAAB20% perovskite films in addition to the 30 nm NAAB layer of solid crystalline imide film. The absorption spectrum of the standard lead-based perovskite PEPB displays the classical narrow absorption peak at 403 nm, indicative of the emission of the inorganic part of the 2-D perovskite structure,^{5,27,35,54} along with the higher energy broad bands (commonly observed) between 200 and 350 nm, attributed to transitions involving higher energy electronic bands.^{57–60}

The absorption spectrum of the fluorophore, that is, of the NAAB imide ammonium salt alone (in the form of a cast film of the NAAB monomer microcrystals), displays the standard 2,3-

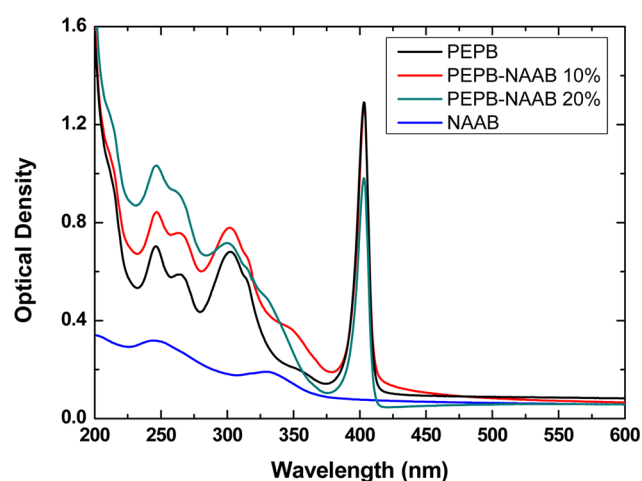


Figure 3. Absorption spectra of PEPB, PEPB-NAAB10%, PEPB-NAAB20%, and NAAB thin layers.

naphthalimide absorption spectrum, featuring two large bands at respectively 250 and 345 nm. It is interesting to notice that the relative absorption coefficients of the imide in the solid form are quite different from their counterpart in solution. Although the absolute values of the absorption coefficients are quite difficult to determine in the solid, due both to the relative error on the film thickness and to the losses by scattering, the absorption coefficients at respectively 250, 340, and 360 nm are in a ratio 3/1.5/1, respectively. In solution they are reported to be 50 000/5000/2500⁶¹ (the values are given approximatively, because they are subject to variations according to the solvent). The solution spectra of NAAB (see Figure S3) does agree with this report.

The absorption spectra of perovskite films containing 20 and 10% in proportion of NAAB (diluted into PEPB) display, as in PEPB, the narrow absorption peak at 403 nm and the features at higher energy are a combination of the absorption of the two components of the film, namely the perovskite and the fluorophore. PEPB-NAAB20% exhibits a less intense absorption peak at 403 nm, coherent with the lower crystallinity of this material, but it can also be noted that, despite the fact that 20% NAAB film displays poor crystallinity, it however shows the inclusion of the organic moiety in the expected proportion. Additionally, it is interesting to remark that, despite the introduction of the fluorophore in the lattice, no shift of the absorption peak can be seen for PEPB-NAAB10%, which is consistent with the fact that the lattice is only weakly perturbed and presents practically no strain.³⁹

Figure 4 shows the photoluminescence spectra of PEPB, PEPB-NAAB10%, and NAAB under different excitation wavelengths, 360, 340, and 250 nm, corresponding to the NAAB absorption maxima. The photoluminescence spectra in Figure 4 show that the PEPB-NAAB10% perovskite emits between ca. 2 and 4 times more photons (in the same irradiation conditions, and according to the excitation wavelength) than the standard PEPB, whatever the excitation wavelength. In addition, we observe that, pleasantly, no electron transfer is observed (otherwise a fast degradation of the material, with local bromine production, would have been observed) that would have been detrimental to the energy transfer. This indicates that, according to our expectations, the excited state of the imide is not a powerful enough oxidant to oxidize the coordinated bromide ions.

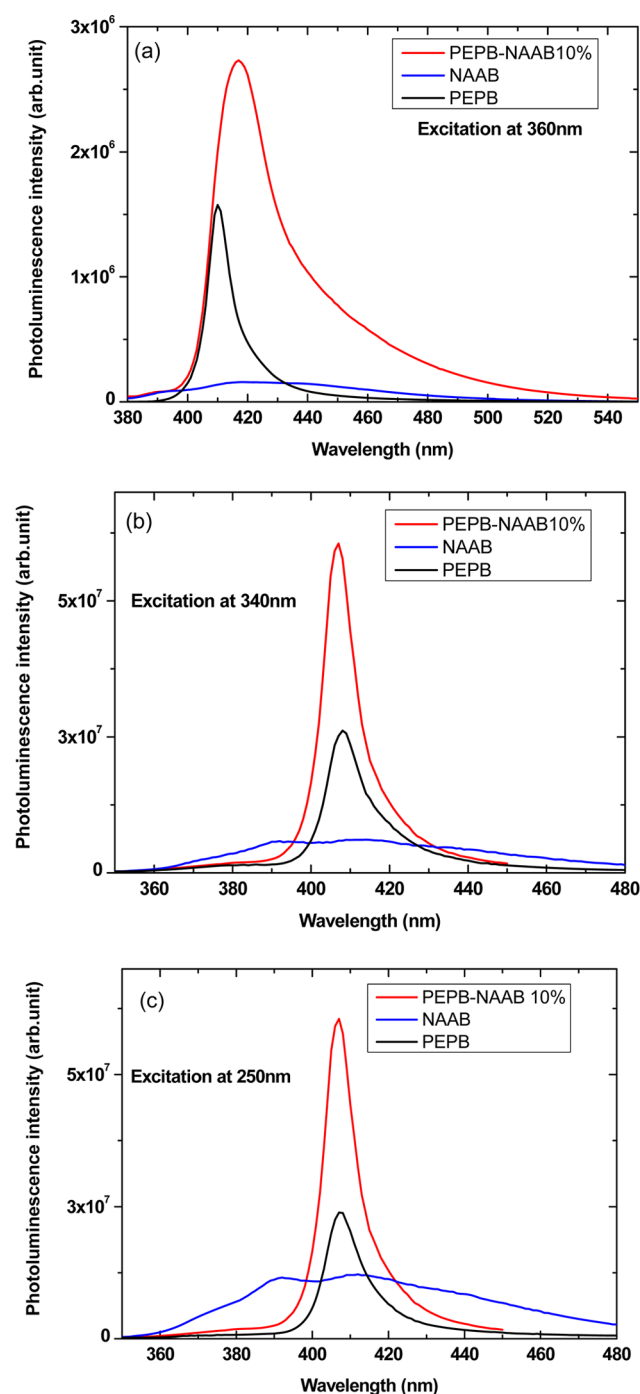


Figure 4. Photoluminescence spectra of the two perovskites PEPB and PEPB-NAAB10% and of the NAAB layer. The excitation wavelength is (a) 360, (b) 340, and (c) 250 nm.

This situation is exemplified by Figure 5, which represents the picture taken of the three deposits PEPB, PEPB-NAAB10%, and NAAB. We measured the scattering for the three deposits: we find that this scattering is low (of the order of magnitude of 1%, see Figure S4,) and is identical in the three cases, at the emission wavelength of the perovskite. This last picture illustrates clearly that, for a given thickness, the fluorophore doped film emits much more light than the other deposits, including the pure imide itself, the emission of which displays a low quantum yield in the solid state.

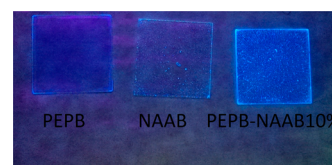


Figure 5. Photograph of the three layers taken under illumination with a standard laboratory lamp (broad band at 360 nm). From right to left: standard PEPB perovskite layer; NAAB microcrystal layer, and 10% NAAB doped PEPB layer.

In Figure 4, no imide emission is registered at its usual emission wavelength around 390 nm,⁶¹ which suggests an efficient energy transfer between the imide molecule acting as an “antenna” and the perovskite “collector”. Figure 6 shows the

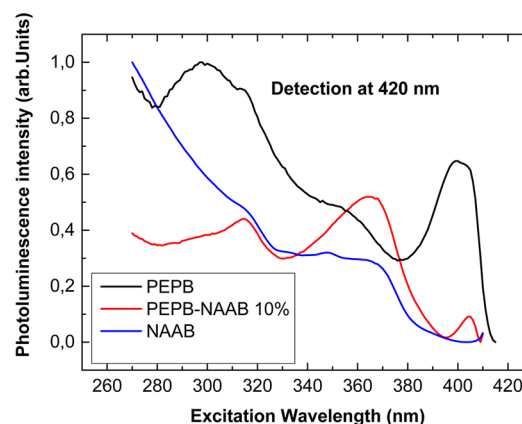


Figure 6. Excitation spectra of photoluminescence of PEPB, PEPB-NAAB10%, and the NAAB layer. The detection wavelength is 420 nm.

excitation spectra of the three samples detected near the maximum of the perovskite photoluminescence peak (detection wavelength is 420 nm). It can be seen that the PEPB-NAAB10% peak around 360 nm appears shifted compared to the PEPB peaks and also shifted compared to the NAAB signal, suggesting also that these shifts are the signature of an interaction between the fluorophore and the perovskite. Unfortunately, because no emission of the imide outside the perovskite emission band can be detected, it was not possible to perform time-resolved spectroscopy in order to detect a change in the relaxation time of the fluorophore in the PEPB-NAAB10% sample, and then irremediably prove the excitation energy transfer and determine its time scale.

We have integrated the area of the photoluminescence peaks shown in Figure 4, for both the standard PEPB perovskite and the 10% NAAB doped sample. The optical density *increases* between PEPB and PEPB-NAAB10% at excitation wavelengths of respectively 250, 340, and 360 nm are respectively of 0.14, 0.15, and 0.12. Assuming a complete energy transfer from the fluorophore to the perovskite, we expect an increase of the photoluminescence by a factor of respectively 1.08, 1.40, and 1.47. (See Table S1 and following discussion for calculation details.) From the photoluminescence spectra, on the other hand, we measure brilliance increases by factors of 2.2, 1.9, and 4.2 for excitation wavelengths at 250, 340, and 360 nm, respectively. This indicates that not only does the imide improve the light collection efficiency of the perovskite, but also, interestingly, the fluorescence yield of the doped perovskite is noticeably increased. This fact is not completely

understood for the moment, but several comments can be given. First, it is possible that the presence of the imide molecule, when its dilution is inferior to 20%, not only tolerates, but stabilizes (has a positive effect) the crystallographic structure of the perovskite: the fact that the X-diffraction spectrum of PEPB-NAAB10% reveals a high crystallinity and that no shift of the excitonic peak can be seen in the absorption spectrum is consistent with the absence of strains in the structure, and can support this assertion.

Another explanation could be also a resonance phenomenon as described in ref 52 where a resonance between the Wannier exciton of $(C_{10}H_7CH_2NH_3)_2PbBr_{1-x}I_x$ perovskite and the Frenkel exciton of the naphthylmethyl moiety has been tuned, leading to the enhancement of the radiative transition rates of the organic moiety. In fact, it can be seen in Figure 6 that, around 360 nm, there exists a near-resonance situation between the PEPB exciton and the NAAB exciton: this could explain the particularly great enhancement (4.2 measured against 1.47 expected(!), much higher than at other wavelengths) of the perovskite emission brilliance for this excitation wavelength. Additionally, it can be noted that the photoluminescence spectrum in Figure 4a (excitation wavelength 360 nm) appears slightly different from the photoluminescence spectra in Figure 4b,c: the luminescence band of PEPB-NAAB 10% is slightly red-shifted with respect to that of PEPB and has a broad tail toward long wavelengths. This broad tail cannot be explained by NAAB photoluminescence, which is really too weak, so we attribute this particular behavior in Figure 4a to the resonance phenomenon.

Figure 7 displays a reasonable energy-level diagram that can reflect coherently the resonance phenomenon. The band

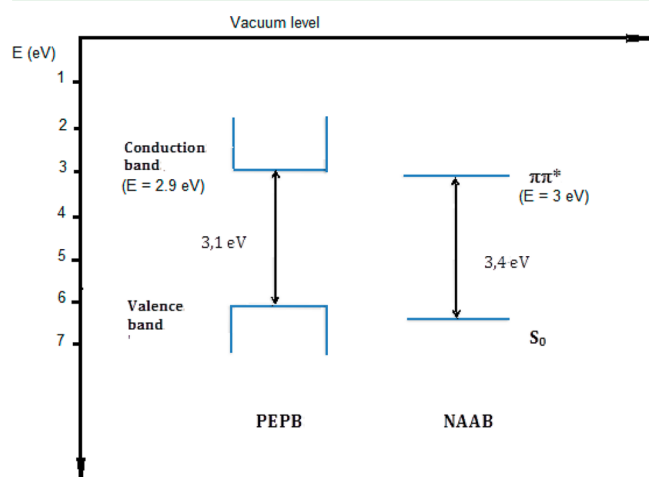


Figure 7. Energy-level diagram.

structure of PEPB has not yet been calculated, and the positions of the conduction and valence bands have not yet been measured as well, but an energy diagram can be found in ref 62 for the perovskite CHEPbBr₄ (CHE = cyclohexenylethylammonium): CHEPbBr₄ and PEPB are two compounds whose optical properties are extremely close to one another; they exhibit the same optical band gap and, additionally, we have demonstrated in ref 27 that the organic part has little influence on the value of the optical band gap; finally, in addition, these organic parts are extremely similar (phenyl for PEPB, and cyclohexenyl for CHEPbBr₄).

On the other hand, the energy gap of NAAB can be found in ref 63: the energy difference between the fundamental singlet state and the excited singlet state is 79.4 kcal·mol⁻¹, that is, 3.4 eV. For the determination of the absolute levels, we can rely on the electrochemical reduction potential of the 2,3-naphthalimide core, which has been measured to be -1.3 V vs the normal hydrogen electrode (-1.82 relative to a Ag/Ag⁺ reference).⁶⁴ We can apply the classical equation linking the redox potentials to the energy levels relative to the vacuum level: $E = -E_{\text{redox}} - 4.3$ eV.⁶⁵ We find an energy level of -3.0 V for the NAAB lowest unoccupied molecular orbital so we can place the NAAB energy levels relative to the valence and conduction bands of PEPB as shown in Figure 7. Following our experimental results, this is quite compatible with a resonance phenomenon between the perovskite and the NAAB molecule.

From this interpretation based on the resonance phenomenon, we also wish to point out that, in addition to the conditions listed in the Introduction (steric hindrance, relative positions of the energy levels to make possible energy transfer, unfavorable photoinduced electron transfer), the choice of the most efficient organic doping luminophore has to take into account the potential existence of resonances between the excitonic states of the organic molecule and the excitonic states of the perovskite.

CONCLUSION

We have demonstrated that it is possible to increase substantially the brilliance of a 2-D perovskite by doping standard bromide-based perovskites with an efficient organic luminophore. We have also discussed how to choose this organic luminophore in order to obtain the best activation of the perovskite brilliance. Once the proof of concept of this activation of the perovskite brilliance is demonstrated, it can probably be done in other spectral ranges, for example in the green range, by working with other perovskites (the iodine ones for the green range) and choosing the suitable luminophores. The doping of the organic-inorganic perovskites with fluorophores can be very interesting to enhance the luminescence efficiency of the perovskites in OLEDs or laser devices. The doping of 3-D perovskites, although certainly more difficult because of the more restrictive conditions linked to the 3-D crystal structure, remains however an attractive goal similarly.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b05279.

Nuclear magnetic resonance measurement of NAAB; absorption spectrum of a solution of pure NAAB in DMF; diffuse reflectance measurement of PEPB and PEPB-NAAB10%; calculated values of the brilliance improvement from measured values of the optical density enhancement (PDF)

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Notes

The authors declare no competing financial interest.

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