

## RESEARCH ARTICLE OPEN ACCESS

# Efficient in-Plane Exciton Transport in a Discontinuous Layered Lead-Bromide Perovskite

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## ABSTRACT

This study reports a new class of two-dimensional lead-bromide perovskite based on monovalent 4-aminomethylbenzoic acid (AMBA) cations featuring a discontinuous inorganic layer. Strong hydrogen-bonding interactions at the interlayer between AMBA molecules impose structural rigidity that prevents the formation of continuous metal-halide layers, instead generating isolated linear islands of three edge-sharing  $[\text{PbBr}_6]^{4-}$  octahedra ( $\text{Pb}_3\text{Br}_{14}$ ). The anisotropic in-plane arrangement of the structure is confirmed by angle-resolved polarized Raman spectroscopy, which reveals directional vibrational modes aligned with the octahedral island orientation. Despite the discontinuous lattice, transient photoluminescence microscopy demonstrates efficient in-plane exciton transport. Transport is strongly anisotropic, with the diffusion coefficient along the *c*-axis ( $0.149 \text{ cm}^2/\text{s}$ ) exceeding that along the *a*-axis ( $0.042 \text{ cm}^2/\text{s}$ ) by over threefold. This anisotropy is attributed to preferential near-field resonant energy transfer between the anisotropically oriented islands, as confirmed by numerical simulations, offering an efficient alternative transport mechanism in discontinuous layered perovskites.

## 1 | Introduction

In recent years, two-dimensional (2D) hybrid organic-inorganic metal halide perovskites (HOIPs) have attracted significant attention for applications in photovoltaics [1, 2], light-emitting diodes

(LEDs) [3], photodetectors [4–6], circularly polarized photoluminescence emission [7], X-ray detectors [8], and lasing devices [9]. Their inherent tolerance to moisture and ion migration provides a pathway to overcome the stability challenges that have limited 3D counterparts [10, 11]. Furthermore, compositional engineering

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of both organic and inorganic components offers fine control over optical, electronic, and structural characteristics, enabling tailored device performance.

The 2D HOIPs consist of an inorganic layer of corner-sharing metal-halide octahedra, with organic spacer cations separating the layers. Depending on the type of spacer cation, 2D HOIPs can be divided into two phases, with the monovalent cations ( $R\text{-NH}_3^+$ ) in Ruddlesden–Popper (RP) perovskites exhibiting a characteristic Van der Waals gap between layers, and bivalent cations ( $(R\text{-NH}_3^+)_2$ ) of in Dion–Jacobson (DJ) perovskites providing a direct link between the inorganic layers. In both classes, through variation in the ratio of the inorganic precursors and the spacer cation, the thickness of the inorganic layer can be tuned providing control over the degree of quantum and dielectric confinement, resulting in control over the excitonic excited state and tunable band gaps [12].

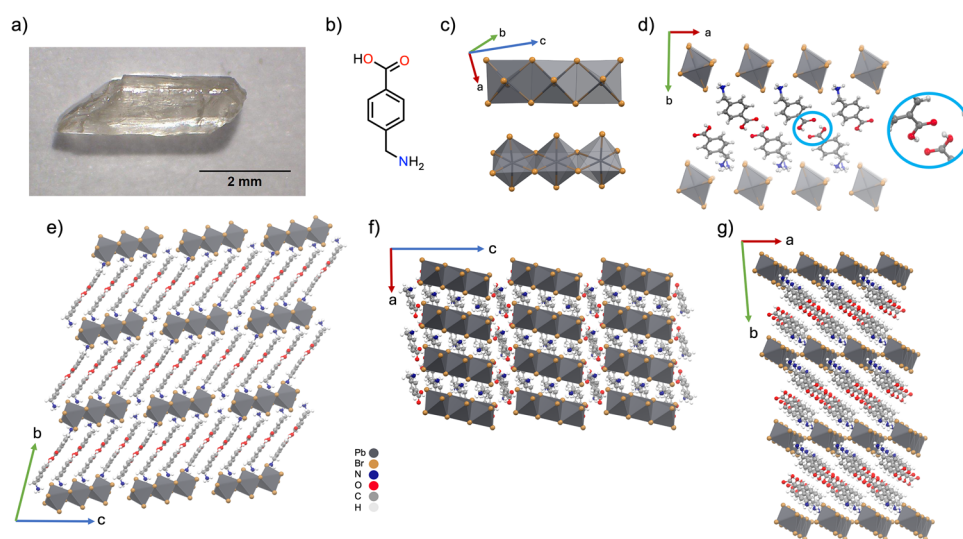
Importantly, in 2D HOIPs, the spacer cation plays a dual role in defining the structural and functional properties of the material [13]. By separating and templating the inorganic metal–halide slabs, the spacer cation contributes significantly to the overall structural rigidity and mechanical stability of the layered architecture. At the same time, its size, shape, and chemical functionality directly affect the octahedral tilting, bond angles, and lattice strain within the inorganic layers [14]. Rigid or bulky spacer cations can impose steric constraints that induce pronounced distortions in the inorganic framework, potentially degrading electronic coupling and charge transport. Excessive rigidity in the organic layer can further hinder the formation of extended inorganic connectivity, favoring the stabilization of lower-dimensional perovskite motifs such as one-dimensional chains or even zero-dimensional isolated octahedra instead of well-connected 2D slabs [15]. Consequently, a certain degree of flexibility in the organic layer is crucial, as it allows the spacer to accommodate lattice mismatch without causing excessive distortions in the inorganic sheets. This balance between rigidity

for structural integrity and flexibility to avoid distortions is therefore essential to minimize unfavorable distortions in the inorganic layers and to optimize the optoelectronic performance of 2D perovskites [16, 17].

Here, we present a new class of 2D HOIPs in which strong hydrogen-bonding interactions between monovalent 4-aminomethylbenzoic acid (AMBA) cations of an RP perovskite lead to a discontinuous 2D plane of  $[\text{PbBr}_6]^{4-}$  octahedra, herein 3Pb-AMBA (CCDC 2519094). We note that a different lead-bromide perovskite phase with a distinct composition has been reported using AMBA as a cation [18]. While the structure obtained from synchrotron single-crystal x-ray diffraction (SCXRD) clearly shows the conventional Van der Waals separation between inorganic layers characteristic of the RP phase,  $[\text{Pb}_3\text{Br}_{14}]^{8-}$  islands of three edge-sharing octahedra are formed in the plane of the material. We show that this anisotropic arrangement of the 2D plane leads to directional vibrational modes. Remarkably, despite the discontinuous 2D plane, transient photoluminescence microscopy reveals efficient in-plane exciton transport, with strongly anisotropic diffusivity that follows the orientation of the  $[\text{Pb}_3\text{Br}_{14}]^{8-}$  islands. The observed anisotropic transfer rates align closely with numerical electromagnetic simulations, supporting near-field resonant energy transfer as the primary transport mechanism.

## 2 | Results and Discussion

Millimeter-sized crystals (Figure 1a and Table S3) were synthesized in concentrated HBr (9M) using a Duran pressure tube and a 1:2 molar ratio of  $\text{PbBr}_2$  to 4-aminomethylbenzoic acid (AMBA, see Figure 1b). The reaction mixture was heated at 115°C for 72 h and subsequently left to cool for 48 h to room temperature, yielding colorless crystals as shown in Figure 1a. We note that exposure to humidity leads to rapid degradation and loss of properties. Once extracted from solution the manipulation of the

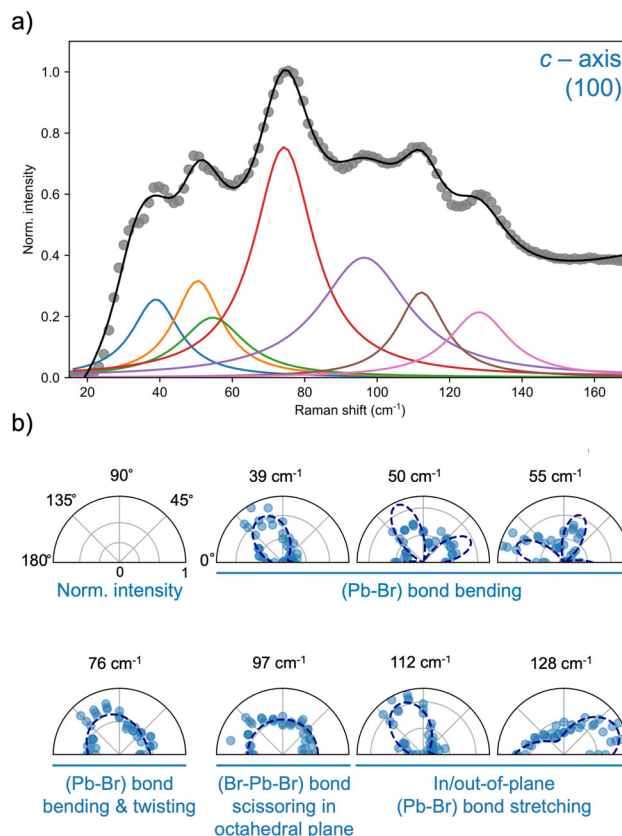


**FIGURE 1** | (a) Crystal of 3Pb-AMBA. (b) Chemical structure of 4-aminomethylbenzoic acid (AMBA). (c) Polyhedral representation of the  $[\text{PbBr}_6]^{4-}$  octahedra forming three edge-sharing octahedra “islands”. (d) Arrangement of the  $[\text{PbBr}_6]^{4-}$  octahedra highlighting the hydrogen bonds between carboxylic groups (blue circles), (e) a view, (f) b view, and (g) c view of the crystal packing showing the spatial distribution of the islands and the AMBA molecules within the extended structure.

crystals was done using non-metallic tools and protected with immersion oil (Nikon) for further characterization.

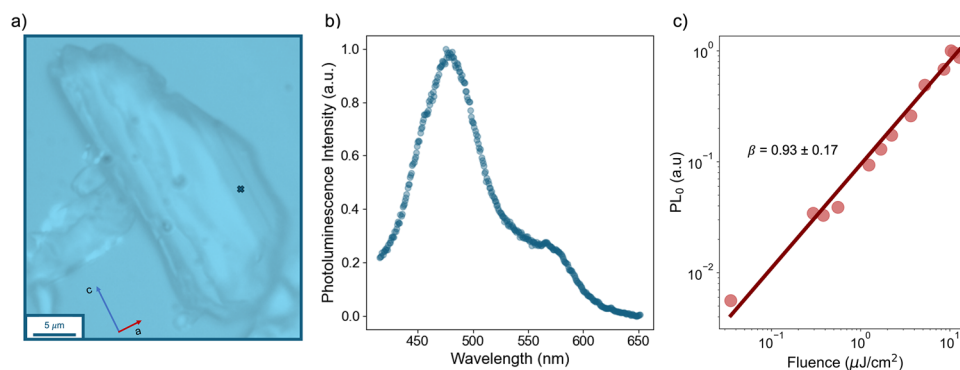
The crystals display a preferential growth direction in the *c*-axis, as shown in Figure 1e. They crystallize in triclinic space group *P* 1 (no. 2) with lattice parameters *a* = 7.7460(16) Å, *b* = 16.707(3) Å, *c* = 16.756(3) Å,  $\alpha$  = 74.96(3)°,  $\beta$  = 86.60(3)°,  $\gamma$  = 84.38(3)°. SCXRD analysis reveals a layered structure in which an arrangement of edge-sharing [PbBr<sub>6</sub>]<sup>4−</sup> octahedra forms isolated groups (islands) of three octahedra (Figure 1c). Each island is separated from its neighbors by organic spacers, a connectivity markedly distinct from the continuous orbital overlap responsible for band-like exciton transport in conventional 2D perovskite sheets. These [Pb<sub>3</sub>Br<sub>14</sub>]<sup>8−</sup> islands interact with the protonated amine groups of AMBA by the NH<sup>3+</sup> to stabilize their negative charge. The angles between apical bromine atoms within each island are 177.75 (2)°–178.06 (2)°, and between lead atoms are 180° (Table S1). The layered structure is built up through hydrogen bonds (O⋯O distances of 2.607(7) and 2.609(8) Å (Figure 1d)) between neighboring carboxylic acids of the interlayer AMBA spacers. We hypothesize that the strong interlayer hydrogen-bonded network imposes a degree of rigidity on the overall structure that prevents the formation of a continuous metal-halide layer. The overall resulting layered structure with the discontinuous 2D plane is illustrated in Figure 1d–g.

To gain more insight into the crystal structure, we performed Raman spectroscopy measurements on crystals at the two accessible crystallographic planes determined by XRD, (100) and (010) (Figure S1). As displayed in Figure 2a, we focus our attention on the low-frequency region (<200 cm<sup>−1</sup>), where Raman spectrum shows 7 modes, which sharpen when lowering the temperature (Figure S2). The Raman signal is similar to those of other edge-sharing [PbBr<sub>6</sub>]<sup>4−</sup> octahedra lattices [19, 20], usually showing intense and blended modes below 150 cm<sup>−1</sup>. In contrast, face-sharing compounds show pronounced modes around 150 cm<sup>−1</sup> and corner-sharing ones present strong and defined modes below 100 cm<sup>−1</sup> [19, 21, 22]. The observed Raman modes can be ascribed to vibrations of the inorganic [PbBr<sub>6</sub>]<sup>4−</sup> octahedra lattice [19, 21, 23]. Concretely, in low-dimensional hybrid PbBr-based perovskites, vibrations at 39, 51, and 55 cm<sup>−1</sup> can be associated to Pb–Br bond bending, 74 cm<sup>−1</sup> to bond bending and twisting, 96 cm<sup>−1</sup> to Br–Pb–Br bond scissoring in the octahedral plane, and 112 and 128 cm<sup>−1</sup> to Pb–Br stretching [23]. To correlate these modes with the crystal orientation, we carried out angle-resolved linearly polarized Raman spectroscopy measurements by rotating the sample under fixed configuration of polarizer and analyzer parallel to each other (VV configuration) [24]. In case of the (100) plane (Figure 2b, see Figure S3 for the (010) plane and further discussion), we observed that several modes show a clear directionality of their intensity as a function of the angle of rotation of the sample, highlighted in the polar plots. Specifically, the angular modulation has a preferential orientation with respect to the alignment of the islands of [Pb<sub>3</sub>Br<sub>14</sub>]<sup>8−</sup> octahedra, matching with the minimum intensity of the angular modulation of 39 and 112 cm<sup>−1</sup> modes and the maximum intensity of 128 cm<sup>−1</sup> mode (see Figure S3a,b for the (010) plane data analysis). As a result, our low-frequency Raman analysis allows us to determine the direction of connection of islands of [Pb<sub>3</sub>Br<sub>14</sub>]<sup>8−</sup> octahedra and distinguish between crystallographic planes.



**FIGURE 2** | (a) Integrated Raman spectrum (VV configuration) of a crystal showing the 7 vibrational modes fitted with a Lorentzian function corresponding to the crystallographic plane (100). (b) Normalized intensity polar plots for each mode as a function of the relative angle,  $\theta$ , between the crystal and the polarization direction of the laser, for the VV configuration. Polar plot scheme is also included, and the normalized mode intensity is given by the length of the radial coordinate. Experimental data are reported as circles. The dashed lines are estimated patterns based on Raman tensor analysis.

Mechanical exfoliation of a 3Pb-AMBA crystal along the interlayer separation of the *b*-plane produces micron-sized flakes with exposed *ac*-planes of multilayer thickness (see Figure 3a and Supporting Information for more details). Photoluminescence (PL) spectroscopy of such flakes reveals a main emission feature at 477 nm (2.6 eV), with a full-width-at-half-maximum (FWHM) of 170 meV (Figure 3b). The photoluminescence lifetime is biexponential with a  $\tau_{\text{eff}}$  of  $1.05 \pm 0.05$  ns (see Figure S7), combined with a modest spectrally integrated quantum yield of <1%. Notably, at higher power, an additional emission peak (observed as shoulder in Figure 3b) appears at 570 nm (2.17 eV) (see Figure S6a for more details). Temperature-dependent bulk PL spectra (see Figures S9 and S10 for more details) reveal that at lower temperatures this lower-energy peak dominates (see Supporting Information for a more detailed discussion). To determine the nature of the excited state, the dependence of the PL emission on excitation power was measured (Figure 3c). The obtained power-law exponent,  $\beta = 0.93 \pm 0.17$ , is close to 1, indicating that the excited state is of excitonic nature [25, 26].



**FIGURE 3** | (a) White light reflectivity image of a micron-sized flake obtained by mechanical exfoliation of a 3Pb-AMBA crystal. The blue marker (x) indicates the region where photoluminescence and transport measurements were performed. (b) Normalized photoluminescence emission spectrum (2.6 eV) under pulsed laser excitation ( $\lambda_{\text{ex}} = 375$  nm). (c) Dependence of the photoluminescence emission at time zero ( $\text{PL}_0$ ) on the excitation power (expressed in fluence). The data are fitted with a power-law function (dark red line), where the reported  $\beta$  represents the exponent.

We now turn to the in-plane transport properties of the material. The temporal and spatial exciton dynamics were investigated using transient photoluminescence microscopy with diffraction limited excitation on the isolated micron-sized flake (see cross in Figure 3a). By placing an avalanche photodiode in the image plane on a motorized stage, we obtain the spatiotemporal broadening of the exciton population along different crystallographic directions (for details, see Characterization in the [Supporting Information](#)).

While fast broadening of the population is observed along the  $c$ -axis (Figure 4a), we observe significantly slower spatial dynamics along the  $a$ -axis (Figure 4b). We can quantify the exciton diffusivity by fitting each temporal slice to a Voigt function, from which we extracted the variance  $\sigma(t)^2$ , of the exciton spatial distribution [27, 28]. The time-dependent broadening of the emission spot corresponds to the mean square displacement (MSD) of the exciton population (Figure 4c). Notably, the exciton diffusivity along the  $c$ -axis (fast axis) is over three times faster than along  $a$ -axis (slow axis). A full polar plot of the diffusivity ( $D$ ) values (Figure 4d) confirms the strong in-plane anisotropy of exciton transport along the  $c$ -axis, highlighting the presence of a preferential transport axis, and is consistent with the preferential growth direction of the crystal. Additional measurements performed at a different position along two orthogonal directions (Figure S5) confirm that the anisotropy is reproducible and is not an artifact of local morphology. Considering the effective lifetime (Figure S7), the average diffusion length along each axis can be calculated by  $L_D = \sqrt{2D\tau_{\text{eff}}}$ , yielding  $177 \pm 7$  nm for the  $c$ -axis and  $88 \pm 5$  nm for the  $a$ -axis. Despite the discontinuous structure of 3Pb-AMBA, these obtained values for the diffusivity and diffusion length are comparable to continuous 2D perovskite materials, falling within the same order of magnitude as  $n = 1$  RP perovskites previously reported [28–30].

Using the Smoluchowski–Einstein relation [31] (Equation (1)), we can calculate the energy transfer rate  $k_{\text{ET}}$  along both the  $a$  and  $c$  direction, considering  $d$  as the distance between the centers of the islands (Figure S8) and the measured diffusivity values  $D$  (Figure 4c):

$$k_{\text{ET}} = \frac{2D}{d^2} \quad (1)$$

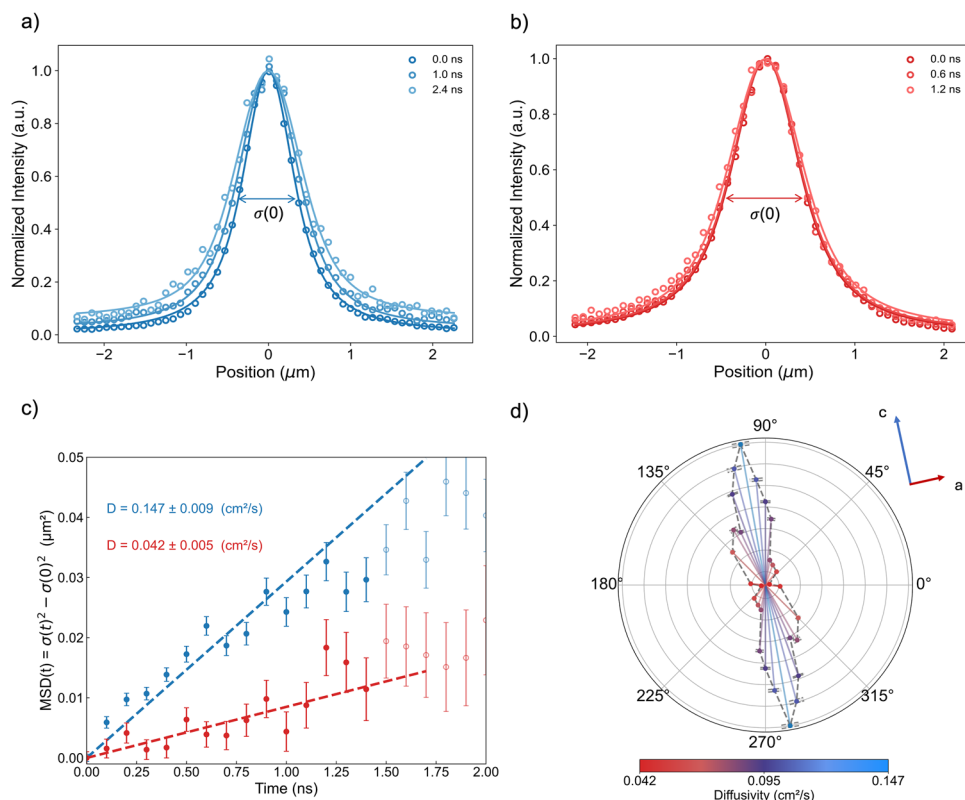
where, yielding energy transfer rates of  $14 \text{ ps}^{-1}$  for the  $a$ -axis ( $d = 0.774$  nm) and  $10.8 \text{ ps}^{-1}$  for the  $c$ -axis ( $d = 1.675$  nm). Consequently, while the longer inter-island distance along the  $c$ -axis gives a slower energy transfer rate, the large distance covered by every step eventually yields a faster diffusivity along this crystallographic direction.

We can compare the experimentally obtained  $a$  and  $c$ -axis energy transfer rates with predictions for dipole–dipole interactions using numerical solutions of Maxwell’s equations using COMSOL Multiphysics. To this, we place an exciton dipole-like source oriented along the  $c$ -axis of one of the islands and numerically evaluate the electric field and Poynting vector, as well as the power absorbed in the neighboring islands. These simulations were parameterized using the crystallographic geometry and the intrinsic anisotropic dielectric function of the islands [32]. As the sub-nanometer island separations place the system outside the point-dipole (Förster) limit, the full near-field simulation, rather than the standard Förster/orientation-factor formula, is needed to capture the observed anisotropy. The contour plot in Figure 5 shows the normalized absorbed power density in the  $ac$ -plane, whose spatial profile follows the electric field intensity.

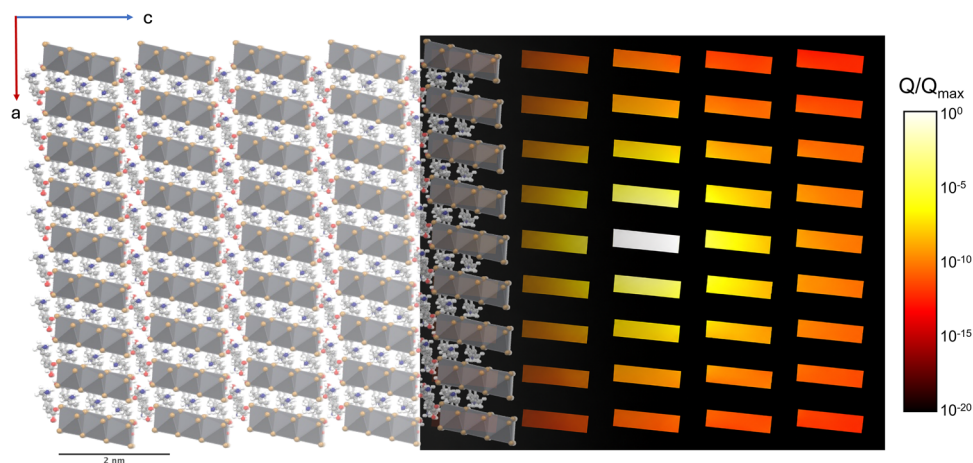
Remarkably, despite the absence of a continuous inorganic sublattice, which rules out the band-like, delocalized transport that is typical in continuous 2D perovskites, transient photoluminescence microscopy reveals efficient in-plane exciton transport, with anisotropic diffusivity that follows the orientation of the  $[\text{Pb}_3\text{Br}_{14}]^{8-}$  islands. Agreement between the measured anisotropic transfer rates and numerical simulations of dipole–dipole coupling indicates that transport instead proceeds via near-field resonant energy transfer between islands, an incoherent, hopping-based mechanism distinct from the coherent band transport of continuous systems.

The energy transfer was computed by integrating the absorbed power density within the volume,  $V$ , of the two first-neighbor islands (along  $c$ - and  $a$ -axes) as:

$$k_{\text{ET}} = \frac{2}{\hbar} \int_V \text{dr} \text{Im}\{\mathbf{E}^*(\mathbf{r}, \omega_e) \mathbf{D}(\mathbf{r}, \omega_e)\} \quad (2)$$



**FIGURE 4** | (a) Normalized intensity profiles of the excited population at different time slices along *c*-axis and (b) *a*-axis. (c) Mean-square displacement of the exciton population over time for *a*-axis and *c*-axis. *D* is the diffusivity obtained by fitting the one-dimensional diffusion equation ( $MSD(t) = 2Dt\alpha$ , with  $\alpha = 1$ ). (d) Polar plot of the diffusivity coefficients obtained along different scans directions.



**FIGURE 5** | Normalized absorption power density  $Q = \text{Im}\{E^*(\mathbf{r}, \omega_e)D(\mathbf{r}, \omega_e)\}$ , profile generated by the exciton dipole-like source present in central inorganic island and oriented along the *c*-axis. Simulation obtained from numerical solutions of Maxwell's equations.

where,  $E(\mathbf{r}, \omega_e)$  and  $D(\mathbf{r}, \omega_e) = \epsilon_0 \epsilon(\mathbf{r}, \omega_e)E(\mathbf{r}, \omega_e)$  are the electric and displacement fields due to the excitonic source, evaluated at the exciton frequency  $\omega_e$ . While a full quantitative analysis would require detailed information about the excitonic dipole strength, we can extract relative energy transfer rates along different directions. From this analysis, we obtain a value of  $k_{ET}$  for the nearest-neighbor transfer along the *a*-axis that is 2.3 higher than that along *c*-axis, in reasonable agreement with the experimentally observed factor of 1.3.

### 3 | Conclusions

In conclusion, we have reported on the synthesis, structural determination, and transport properties of 3Pb-AMBA. While the structure of the material has the overall characteristics of a Ruddlesden–Popper perovskite with Van der Waals interlayer interactions, a discontinuous inorganic layer is obtained with the formation of islands of three edge-sharing  $[PbBr_6]^{4-}$  octahedra, physically isolated from neighboring islands by the organic spacer

layer, markedly distinct from the continuous orbital overlap responsible for band-like exciton transport in conventional 2D perovskite sheets. Angle-resolved linearly polarized Raman spectroscopy measurements show directional modes associated with the anisotropic orientation of the inorganic lattice. Transient photoluminescence measurements reveal an anisotropic in-plane transport consistent with the crystallographic orientation of the material, with markedly higher diffusivity along the *c*-axis as compared to the *a*-axis. Close agreement between the observed anisotropic energy transfer rates and numerical electromagnetic simulations supports a near-field resonant energy transfer as the dominant transport mechanism.

Surprisingly, the measured exciton diffusion constant along the *c*-axis of 3Pb-AMBA (0.149 cm<sup>2</sup>/s) is comparable to that of continuous Ruddlesden–Popper perovskites, such as, for example, (PEA)<sub>2</sub>PbBr<sub>4</sub> (0.2 cm<sup>2</sup>/s) [27], despite its discontinuous lattice. It is important to note though, that in conventional perovskites, the transport mechanism is band-like and hampered by large polaron formation [28]. Our work highlights the potential for near-field resonant energy transfer as an efficient alternative for in-plane energy transport in discontinuous, yet closely packed layered perovskites. This work demonstrates that efficient, anisotropic exciton transport in a 2D perovskite need not rely on the continuous, band-like conduction pathway that is common in these systems. Instead, a hopping-type, near-field resonant mechanism between structurally isolated inorganic islands can achieve diffusion lengths comparable to continuous systems, establishing dipole-dipole coupling as a viable alternative transport pathway in low-dimensional perovskites and opening a route to engineer transport independently of lattice connectivity.

## Author Contributions

**Raquel Utrera-Melero:** conceptualization, investigation, data curation, writing – review and editing. **Antonella Cutrupi:** investigation, data curation, writing – review and editing. **Ivan Rivilla:** investigation, data curation, writing – review and editing. **Davide Spirito:** investigation, data curation, writing – review and editing. **E. Carolina Sañudo:** investigation, data curation, writing – review and editing. **Juan Cabanillas-González:** investigation, data curation, writing – review and editing. **Antonio I. Fernández-domínguez:** investigation, data curation, writing – review and editing. **Beatriz Martín-García:** investigation, conceptualization, data curation, writing – review and editing. **Jose Sánchez Costa:** conceptualization, investigation, data curation, writing – review and editing. **Ferry Prins:** conceptualization, investigation, data curation, writing – review and editing.

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## Conflicts of Interest

The authors declare no conflicts of interest.

## Data Availability Statement

The data sets used in this study are openly accessible via the following link <https://doi.org/10.21950/HIB4U2>. The code used for data processing and analysis is available at <https://github.com/phond-uam/discontinuous-layered-lead-bromide-perovskites>.

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## Supporting Information

Additional supporting information can be found online in the Supporting Information section.

**Supporting File:** adma75282-sup-0001-SupMat.pdf.