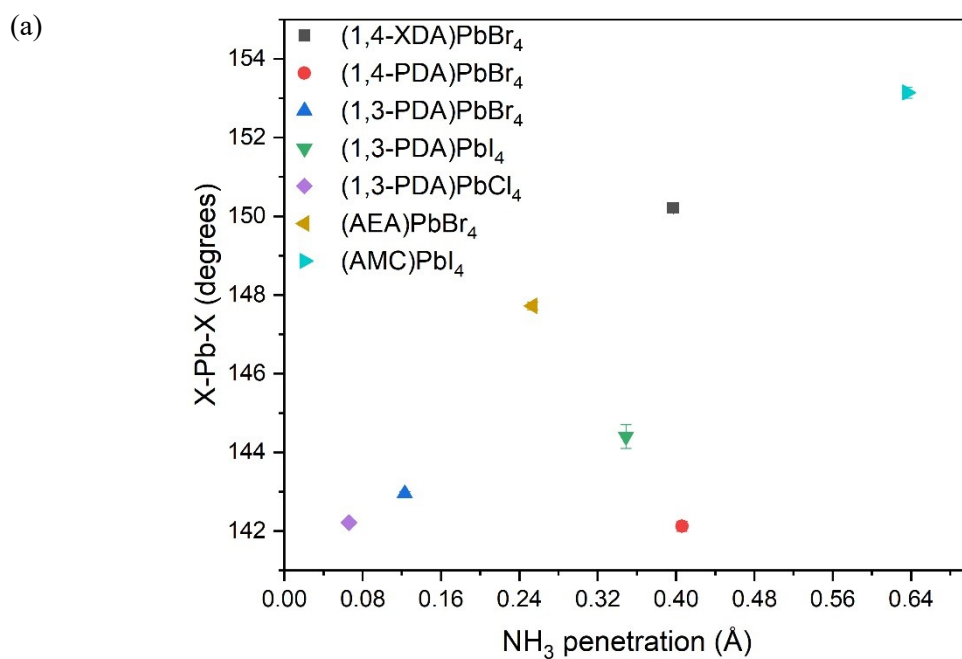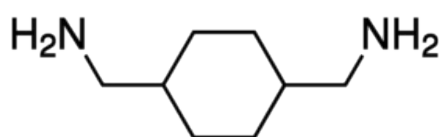**ELECTRONIC SUPPLEMENTARY INFORMATION**

Templating Effect of Diammonium Cations on the Structural and Optical Properties of Lead Bromide Perovskites: a Guide to Design Broad Light Emitters
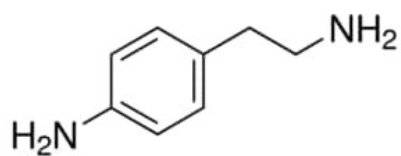
(a)

(b)

AMC

(c)

AEA

Figure S1- (a) Variation of the Pb−X−Pb bond angle as a function of NH$_3$ penetration; (b) molecular structure of 1,4-bis(ammoniomethyl)cyclohexane, and (c) molecular structure of 3-(2-ammonioethyl)anilinium.
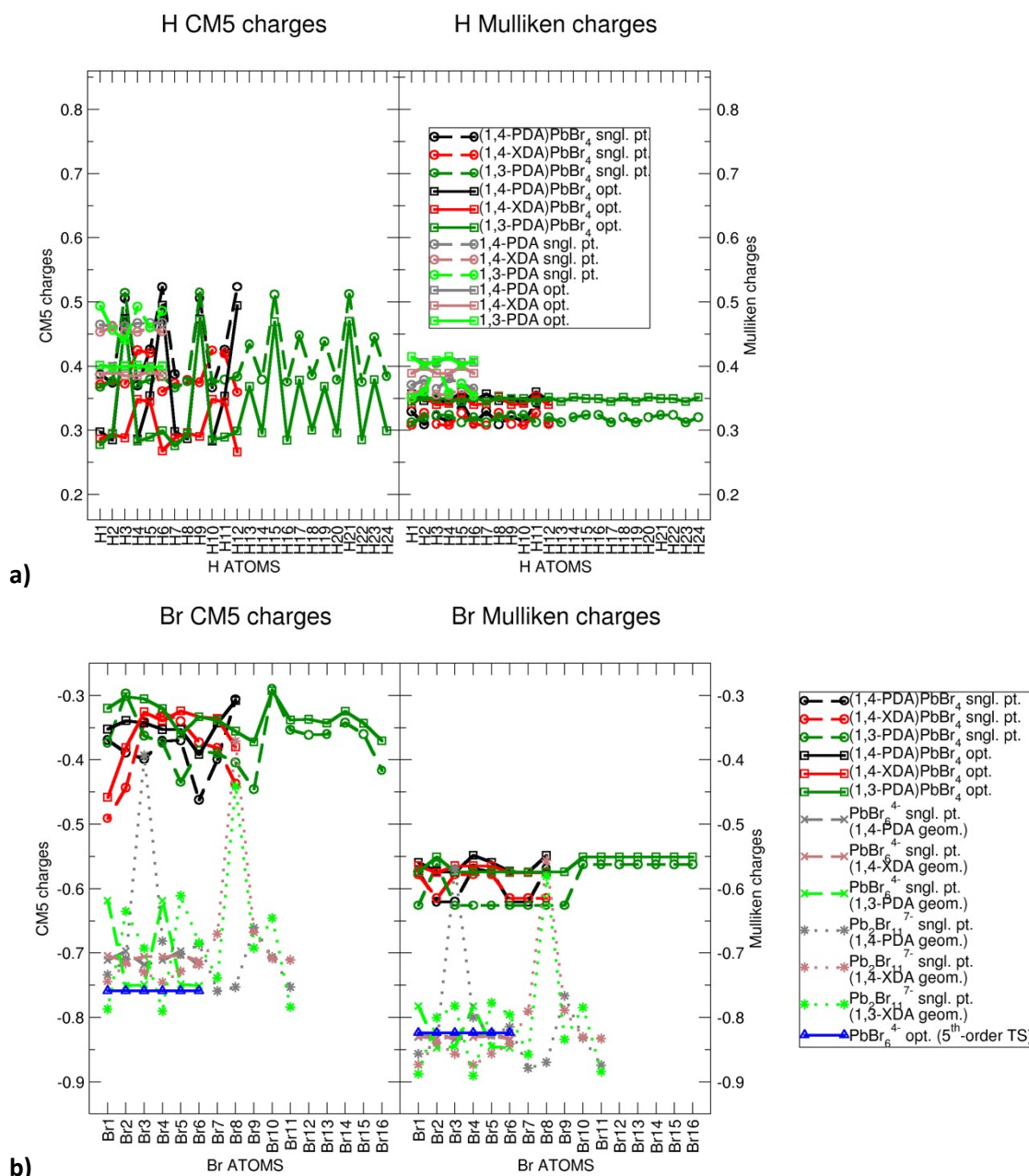
Figure S2. Charges on (a) aminic H and (b) Br of various systems compared in this work as calculated by the CM5 (a, left; b, left) and Mulliken (a, right; b, right) methods at the HSE06/SDD/6-31G(d,p) level of DFT (see SI Materials and Methods below for details). More specifically, charges on perovskites (1,4-PDA)PbBr$_4$ (black), (1,4-XDA)PbBr$_4$ (red), and (1,3-PDA)PbBr$_4$ (green), are calculated both after single-point energy calculations (dotted lines, circles), and after optimization (solid lines, squares). Charges on isolated diammonium cations 1,4-PDA^{2+} (gray), 1,4-XDA^{2+} (pink), 1,3-PDA^{2+} (light green) (panel a only) are calculated both after single-point energy calculations in the gas phase (on perovskite-distorted geometries; dotted lines, circles) and after optimization (solid lines, squares). Charges on isolated [PbBr$_6$]$^{4-}$ (dotted lines, x) and [Pb$_2$Br$_{11}$]$^{7-}$ octahedra (shorter dotted lines, *; panel b only) are calculated only after single-point energy calculations in the gas phase on their (1,4-PDA)PbBr$_4$ (gray), (1,4-XDA)PbBr$_4$ (pink), and (1,3-PDA)PbBr$_4$ (light green) geometries. Charges have also been calculated on [PbBr$_6$]$^{4-}$ (solid blue line, blue triangles, panel b), which optimizes in the gas phase to an octahedral 5th-order transition state (TS). H1-H24 and Br1-Br16 (x-axes) denote individual atoms, as *Gaussian16* uses several replicas of the unit cell to recreate whole molecules: note that this atom numbering does not match the one in crystallographic data. Fluctuations on certain H atoms in perovskites are an artifact (*see SI explanation). Ranges of the y-axes are identical in all panels. Calculations are available electronically.

*As a note of caution, the more notable fluctuations in CM5 charges[11] observed for certain H atoms in single-point and optimized (1,4-PDA)PbBr$_4$ and (1,3-PDA)PbBr$_4$ (panel a, black and green lines, respectively) should be disregarded: they refer to individual H atoms H3, H6, H9, H12 in the former case, and H atoms H3, H9, H14, H21 in the latter case, which get "cut" by *Gaussian16* when recreating the minimal cell necessary for the calculation, and are assigned slightly larger charges as a result of a flaw in *Gaussian16*'s partitioning of the electron density under periodic boundary conditions. Such effect is not observed with Mulliken charges.[12]

With this *caveat* in mind, it is evident across all cases studied that Br and H charges fluctuate over a ~0.2e range (or smaller) in all scenarios, and that perovskite charges overlap in all cases; in other words, there is no systematic increase or decrease in any one particular perovskite.

Other interesting aspects to note:

- Charge transfer from Br to H upon perovskite formation is consistently reproduced.
- In double octahedra [Pb$_2$Br$_{11}$]$^{7-}$ (see description in SI Materials and Methods), the vertex-shared Br$^-$ (Br3 in the 1,4-PDA(PbBr$_4$) distortion; Br8 in the other two cases) is consistently assigned smaller negative charges, which approach values close to those assigned in the perovskites.
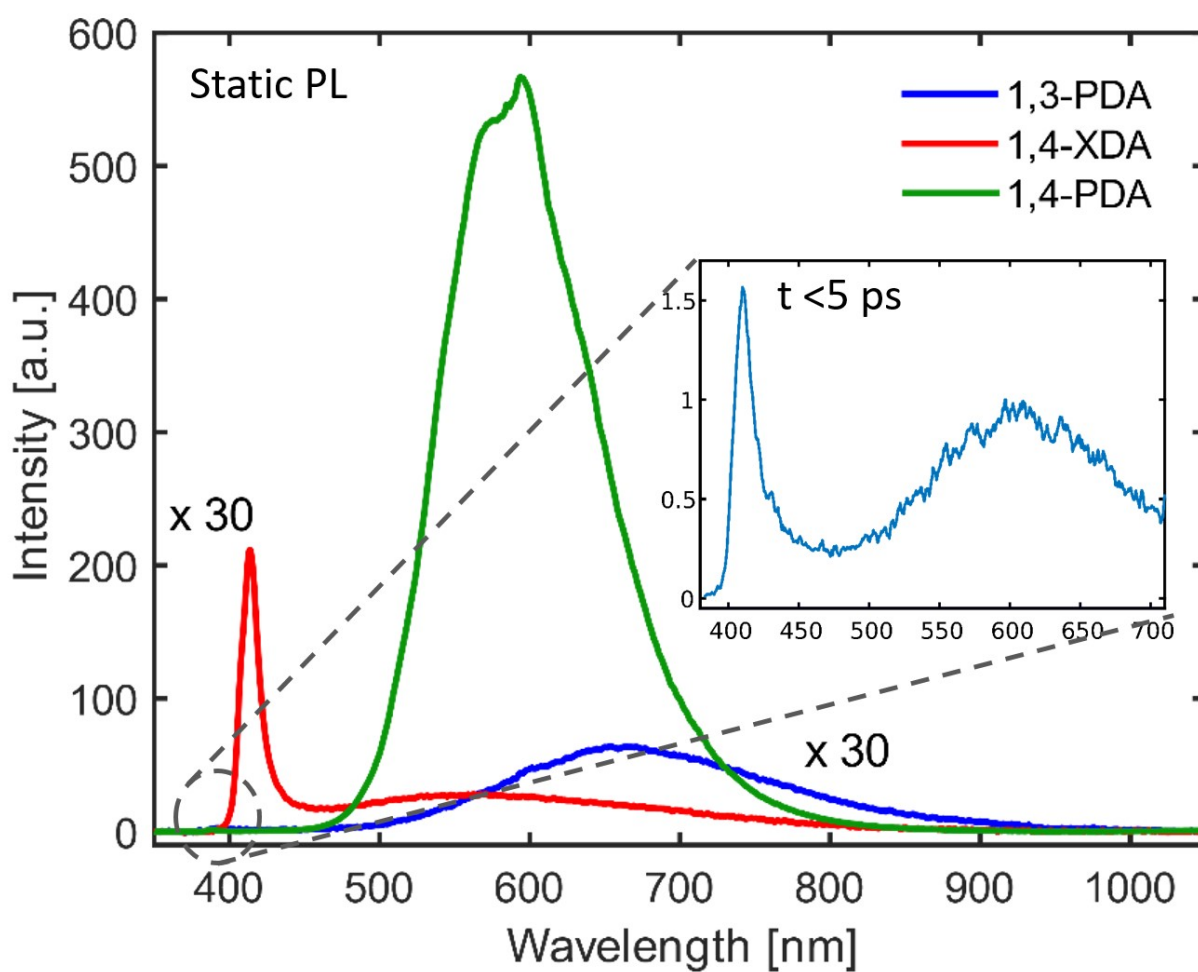
Figure S3: comparison between static photoluminescence spectra at 77K. Inset: spectrum of   1,3-PDA at 77K during the first 5 ps of emission (retrieved from high resolution time resolved data), highlighting the feature at 420 nm which is particularly prominent at early decays.

Figure S4: Fluence-dependent photoluminescence spectra at 77K of: a)1,3-PDA b)1,4-PDA c)1,4-XDA. All spectra are recorded using λ_{ex} of 355nm pulsed laser (1Khz)

Figure S5:1,4-XDA PL evolution in time using a λ_{ex} of 355nm pulsed laser (1Khz) at 2000uW

Figure S6: Time resolved spectra in ns (left) and ps (right) time range of sample a,b) 1,4-XDA c,d) 1,3-PDA and e,f) 1,4-PDA

Materials and methods

Synthesis

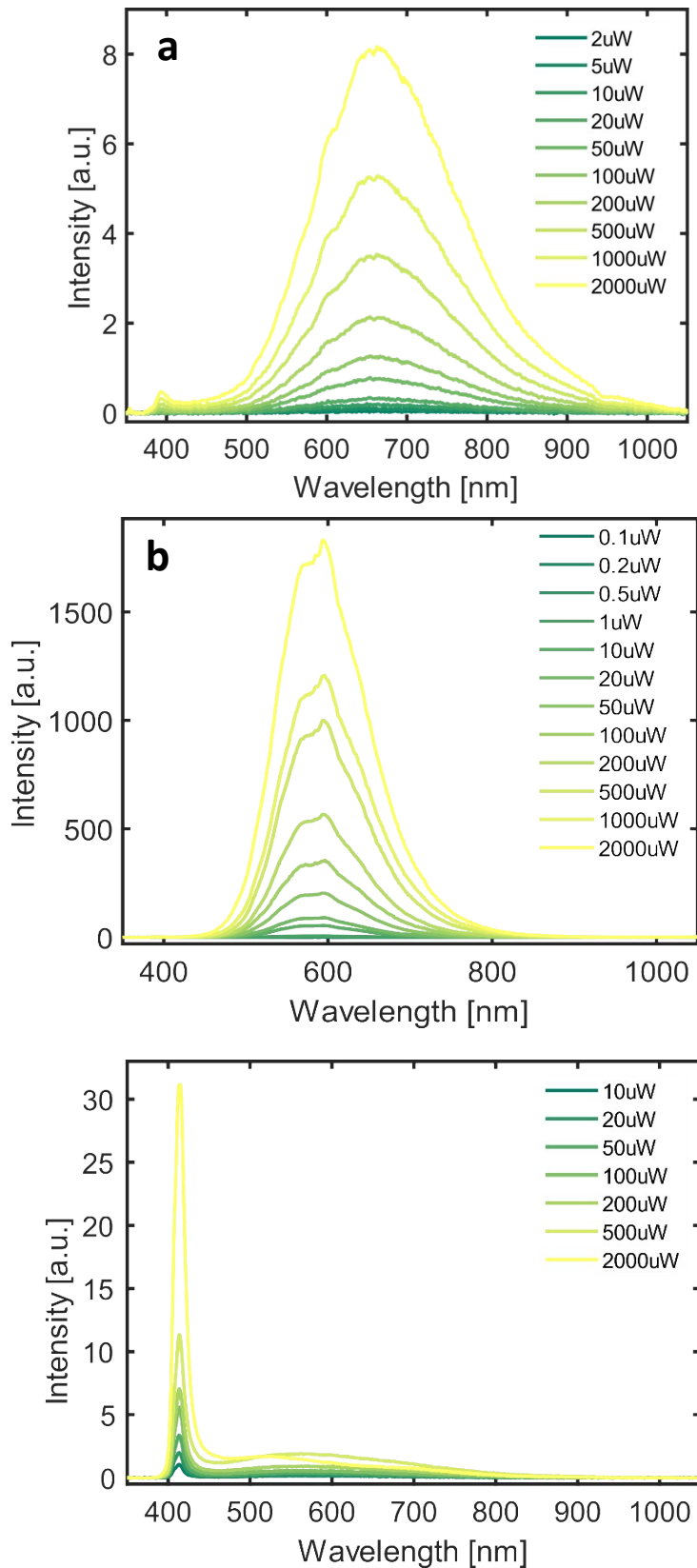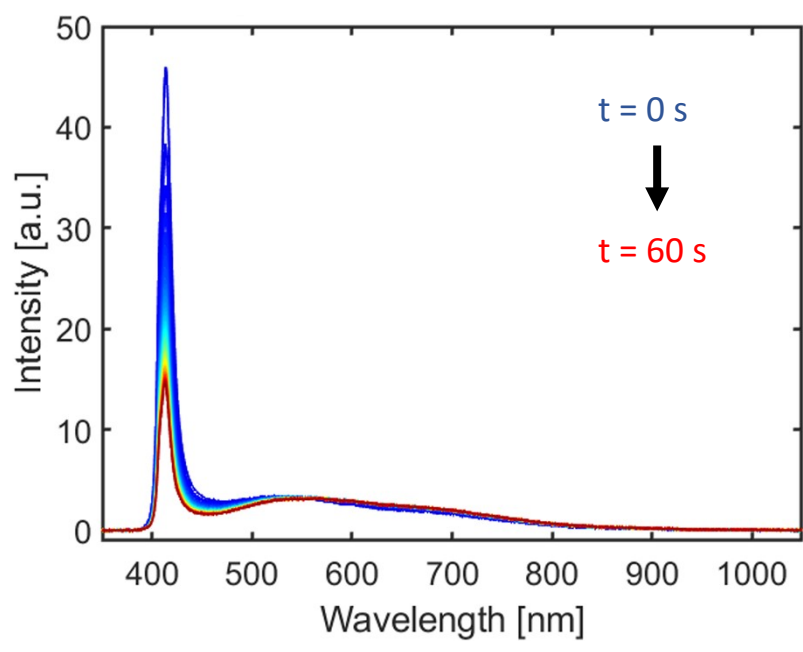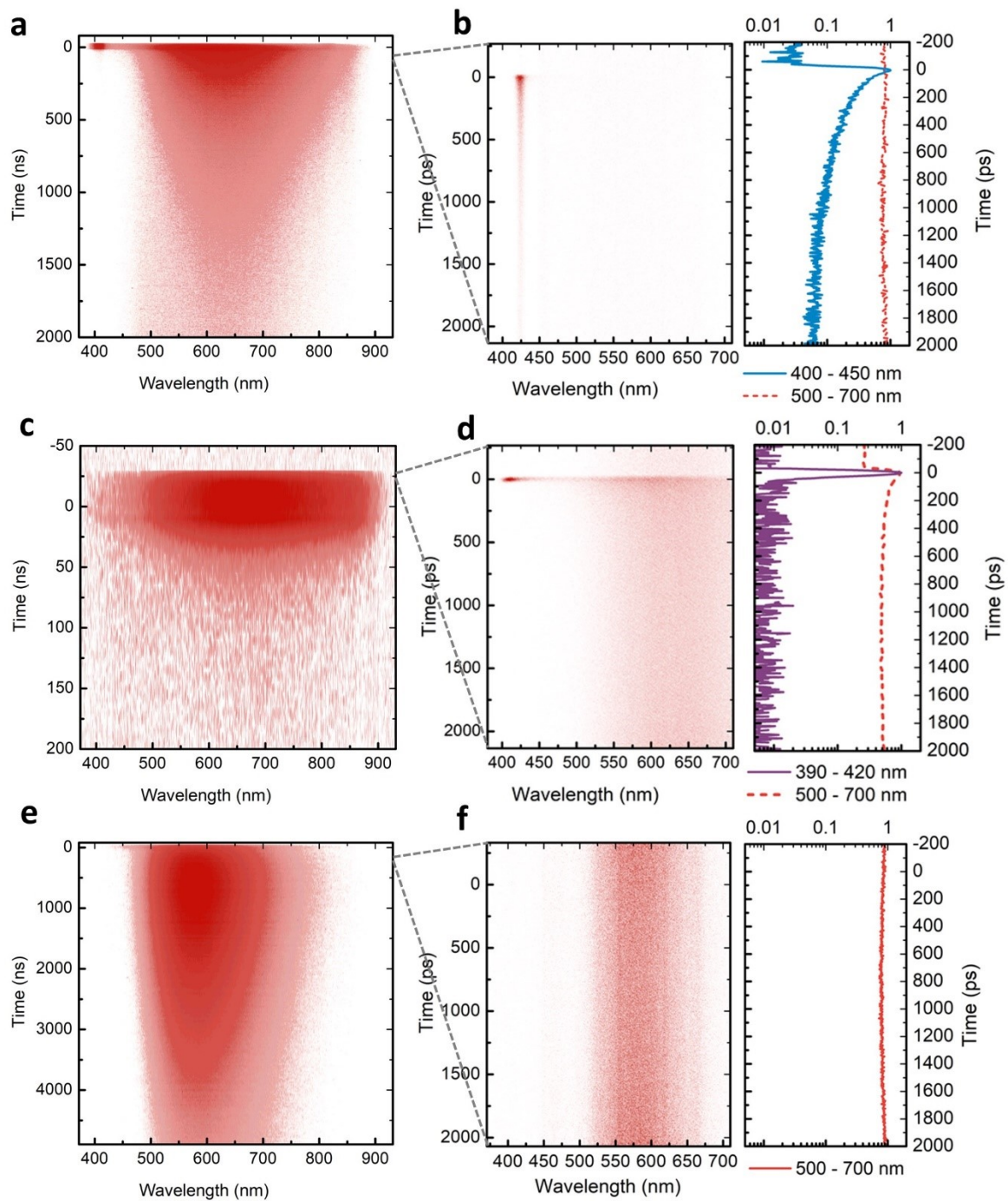Single crystals of (1,3-PDA)PbBr$_4$, (1,4-PDA)PbBr$_4$, (1,3-XDA)PbBr$_4$ and (1,4-XDA)PbBr$_4$ were grown by dissolving a proper amount of lead(II) acetate powder in a large excess of 48% w/w aqueous HBr and 50% w/w aqueous H$_3$PO$_2$, heating the mixture to boiling point. After the solid dissolution, the stoichiometric amount of the solid diamine (liquid for the 1,3-XDA) was added. The crystals formation was obtained by a slow cooling down to room temperature at 2°C h^{-1}.

Single crystal and powder X-ray diffraction

Single crystal data collections ($\lambda = 0.71073$ Å) were performed using a Bruker D8 Venture with Cu and Mo microfocus X-ray sources and PHOTON II detector with Bruker APEX3 program. The Bruker SAINT software[1] was used for integration and data reduction, while absorption correction was performed using SADABS-2016/2[2]. Crystal structures (CCDC) were solved and refined using SHELXT 2014/5 and SHELXL 2018/3[3,4].

XRD measurements on powdered samples were performed using a Bruker D8 Advance in Bragg–Brentano geometry under Cu Kα radiation.

Static and time-resolved photoluminescence

Powder sample preparation: the spectroscopic characterization was performed on perovskite powder samples encapsulated between 1mm glasses.

Static Photoluminescence: Temperature and pump fluence-dependent measurements were performed under vacuum using a Linkam Stage cooled with liquid nitrogen, exciting the sample with the third harmonic (355 nm) from a Nd:YAG Picolo-AOT laser (pulse length of approximately 1000 ps, 1 kHz repetition rate) focused on the sample with a 10 cm lens. PL was detected using a Maya1000 visible spectrometer.

Time-resolved PL: The same light source as for static temperature dependent measurements (Picolo AOT at 355 nm) was used for time-resolved photoluminescence measurements on ns timescale. Measurements were performed under vacuum using a Linkam Stage cooled with liquid nitrogen. The PL was detected with an Andor iStar 320T ICCD camera coupled to a Shamrock 303i spectrograph using a temporal step size of 1 ns for sample (1,3-PDA)PbBr$_4$ and 10ns for (1,4-PDA)PbBr$_4$ and (1,4-XDA)PbBr$_4$ with a spectral resolution of 0.55 nm. The integration ranges used for the broad PL components are: 500 – 700 nm (1,4-PDA), 450 - 700 nm (1,4-XDA), 500-800 nm (1,3-PDA).

TRPL of the excitonic feature in the ps range was performed using a Hamamatsu streak camera and a Coherent Chameleon oscillator (pulse duration 30 fs, repetition rate 80 MHz) as a pump, using a pump wavelength λ = 360 nm obtained by frequency doubling the fundamental at 780 nm in a BBO crystal. The measurements were performed using a measurement window 2000 ps long for all samples (temporal resolution 10 ps), while the fast component of 1,3-PDA was measured in a 180 ps window with the highest available temporal resolution (3.5 ps). The integration ranges used for the narrow PL components are: 400 - 450 nm (1,4-XDA), 390-420 nm (1,3-PDA).

Arrhenius Fit

To estimate the activation energy of non-radiative recombination pathways we fit the PL intensity of the principal emission vs Temperature with an Arrhenius curve (Equation S1)

$$I(T) = \frac{I_0}{1 + C\ exp\left(-\dfrac{\Delta E}{k_B T}\right)}$$

(S1)

where I_0 is the maximum of the intensity, ΔE is the activation energy for the non-radiative recombination pathway and C is the frequency factor[5].

DFT Calculations

Density Functional Theory (DFT) calculations were performed with the *Gaussian16* package,[6] taking also advantage of *Gaussian16*'s implementation of solid-state calculations. Partly in line with recent recommendations by Das *et al.* for Pb-Br perovskites,[7] the chosen density functional was HSE06.[8,9] To model lead(II) electrons, we employed a Stuttgart-Dresden pseudopotential and basis set,[10] whereas electrons on remaining atoms were modelled in full with a 6-31G(*d,p*) basis set. Grids of approximately 750 *k*-points were requested for solid-state calculations. Charge distribution was assessed using both the *Charge Model 5* (CM5) and Mulliken population analysis methods.[11,12] All calculations are available electronically, in a separate zipped folder.

Figure S2 shows the charge distribution (CM5,[11] Mulliken)[12] on aminic protons (panel a) and bromide (panel b) in a variety of situations, as calculated by density functional theory at the HSE06[8,9]/SDD[10]/6-31G(*d,p*) level:

- (1,4-PDA)PbBr$_4$:
    - Single-point energy calculation, experimental structure (dotted black line; black circles).
    - Geometry optimization (solid black line; black squares).
- (1,4-XDA)PbBr$_4$:
    - As above (red replaces black).
- (1,3-PDA)PbBr$_4$:
    - As above (green replaces red).
- 1,4-PDA^{2+} (Figure S2a only):
    - Single-point energy calculation, gas phase, experimental perovskite structure (dotted gray line; gray circles).
    - Geometry optimization, gas phase (solid gray line; gray squares).
- 1,4-XDA^{2+} (Figure S2a only):
    - As above (salmon replaces gray)
- 1,3-PDA^{2+} (Figure S2a only):
    - As above (light green replaces salmon)
- Distorted [PbBr$_6$]$^{4-}$ octahedron—(1,4-PDA)PbBr$_4$ geometry (Figure S2b only):

- o   Single-point energy calculation, gas phase (dotted gray line; gray x).
- Distorted $[PbBr_6]^{4-}$ octahedron—(1,4-XDA)$PbBr_4$ geometry (Figure S2b only):
  - o   As above (salmon replaces gray)
- Distorted $[PbBr_6]^{4-}$ octahedron—(1,3-PDA)$PbBr_4$ geometry (Figure S2b only):
  - o   As above (light green replaces salmon)
- Distorted $[Pb_2Br_{11}]^{7-}$ octahedron—(1,4-PDA)$PbBr_4$ geometry (Figure S2b only):
  - o   Single-point energy calculation, gas phase (shorter dotted gray line; gray *).
- Distorted $[Pb_2Br_{11}]^{7-}$ octahedron—(1,4-XDA)$PbBr_4$ geometry (Figure S2b only):
  - o   As above (salmon replaces gray)
- Distorted $[Pb_2Br_{11}]^{7-}$ octahedron—(1,3-PDA)$PbBr_4$ geometry (Figure S2b only):
  - o   As above (light green replaces salmon)
- $[PbBr_6]^{4-}$ octahedron, optimized in the gas phase to a 5th order transition state – (Figure S2b only; solid blue line; blue triangles; further optimization to a minimum leads to a tetrahedral $[PbBr_4]^{2-}$ and 2 isolated Br$^-$).

Single crystal data refinement

(1,3-PDA)PbBr$_4$

Br$_4$Pb·C$_6$H$_{10}$N$_2$	$F(000) = 1128$
$M_r = 636.99$	$D_x = 3.116$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 21.784$ (7) Å	Cell parameters from 8793 reflections
$b = 8.821$ (3) Å	$\theta = 2.5–28.9°$
$c = 7.398$ (3) Å	$\mu = 24.16$ mm^{-1}
$\beta = 107.214$ (9)°	$T = 303$ K
$V = 1357.8$ (8) Å^3	Plate, dull dark brown
$Z = 4$	$0.2 \times 0.15 \times 0.05$ mm

Data collection

Bruker SMART APEX2 area detector diffractometer	1341 independent reflections
Radiation source: microfocus sealed X-ray tube, Incoatec Iμs	1073 reflections with $I > 2\sigma(I)$
Mirror optics monochromator	$R_{int} = 0.024$
Detector resolution: 7.9 pixels mm^{-1}	$\theta_{max} = 28.8°$, $\theta_{min} = 2.5°$
ω and ϕ scans	$h = -29\rightarrow15$
Absorption correction: multi-scan	$k = -11\rightarrow3$
$T_{min} = 0.496$, $T_{max} = 0.746$	$l = -7\rightarrow8$
1712 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: dual
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.035$	H-atom parameters constrained
$wR(F^2) = 0.090$	$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
1341 reflections	$\Delta\rangle_{max} = 0.95$ e Å^{-3}
63 parameters	$\Delta\rangle_{min} = -1.03$ e Å^{-3}
0 restraints	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Pb01	0.750000	0.750000	0.500000	0.03090 (16)
Br02	0.61047 (4)	0.66824 (9)	0.36323 (18)	0.0496 (3)
Br03	0.77138 (5)	0.56542 (12)	0.18312 (19)	0.0543 (3)
C005	0.500000	0.2998 (12)	0.250000	0.036 (3)
H005	0.500000	0.405267	0.250000	0.043*
C006	0.500000	-0.0124 (11)	0.250000	0.056 (5)
H006	0.500000	-0.117877	0.250000	0.067*
C2	0.4444 (4)	0.2192 (8)	0.1713 (16)	0.035 (2)
C4	0.4440 (4)	0.0640 (8)	0.1678 (17)	0.047 (3)
H4	0.406302	0.011287	0.110473	0.056*
N1	0.3836 (3)	0.2976 (8)	0.0828 (15)	0.052 (3)
H1A	0.376686	0.301131	-0.041922	0.062*
H1B	0.385634	0.391543	0.128178	0.062*
H1C	0.351607	0.247886	0.108242	0.062*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb01	0.0324 (2)	0.0277 (2)	0.0310 (4)	-0.00035 (14)	0.00691 (18)	-0.00391 (17)
Br02	0.0349 (4)	0.0350 (4)	0.0735 (10)	0.0017 (3)	0.0076 (5)	-0.0007 (4)
Br03	0.0529 (5)	0.0656 (6)	0.0486 (10)	-0.0122 (4)	0.0215 (5)	-0.0244 (5)
C005	0.035 (6)	0.031 (4)	0.045 (11)	0.000	0.018 (6)	0.000
C006	0.033 (6)	0.021 (4)	0.120 (17)	0.000	0.030 (8)	0.000
C2	0.033 (4)	0.032 (3)	0.039 (8)	0.005 (3)	0.007 (4)	0.004 (3)
C4	0.032 (4)	0.030 (3)	0.077 (10)	-0.005 (3)	0.016 (4)	-0.005 (4)
N1	0.037 (4)	0.037 (3)	0.071 (9)	0.003 (3)	0.002 (4)	0.008 (4)

Geometric parameters (Å, °)

Pb01—Br02^i	2.9936 (12)	C006—H006	0.9300
Pb01—Br02	2.9937 (12)	C006—C4^{iv}	1.368 (10)
Pb01—Br03^{ii}	3.0692 (13)	C006—C4	1.368 (10)

Pb01—Br03	3.0016 (14)	C2—C4	1.370 (10)
Pb01—Br03[iii]	3.0692 (13)	C2—N1	1.465 (10)
Pb01—Br03[i]	3.0015 (14)	C4—H4	0.9300
C005—H005	0.9300	N1—H1A	0.8900
C005—C2[iv]	1.376 (10)	N1—H1B	0.8900
C005—C2	1.376 (10)	N1—H1C	0.8900
Br02[i]—Pb01—Br02	180.0	C2—C005—H005	121.1
Br02—Pb01—Br03	88.97 (3)	C2—C005—C2[iv]	117.8 (10)
Br02[i]—Pb01—Br03[iii]	86.39 (3)	C4—C006—H006	119.5
Br02[i]—Pb01—Br03[i]	88.97 (3)	C4[iv]—C006—H006	119.5
Br02—Pb01—Br03[ii]	86.39 (3)	C4[iv]—C006—C4	121.0 (10)
Br02—Pb01—Br03[i]	91.03 (3)	C005—C2—N1	120.7 (7)
Br02—Pb01—Br03[iii]	93.61 (3)	C4—C2—C005	121.6 (8)
Br02[i]—Pb01—Br03	91.03 (3)	C4—C2—N1	117.7 (8)
Br02[i]—Pb01—Br03[ii]	93.61 (3)	C006—C4—C2	119.0 (8)
Br03[ii]—Pb01—Br03[iii]	180.0	C006—C4—H4	120.5
Br03—Pb01—Br03[ii]	79.32 (3)	C2—C4—H4	120.5
Br03—Pb01—Br03[iii]	100.68 (3)	C2—N1—H1A	109.5
Br03[i]—Pb01—Br03	180.0	C2—N1—H1B	109.5
Br03[i]—Pb01—Br03[iii]	79.32 (3)	C2—N1—H1C	109.5
Br03[i]—Pb01—Br03[ii]	100.68 (3)	H1A—N1—H1B	109.5
Pb01—Br03—Pb01[v]	142.95 (4)	H1A—N1—H1C	109.5
C2[iv]—C005—H005	121.1	H1B—N1—H1C	109.5
C005—C2—C4—C006	2.1 (16)	C4[iv]—C006—C4—C2	-1.0 (8)
C2[iv]—C005—C2—C4	-1.1 (8)	N1—C2—C4—C006	-179.8 (9)
C2[iv]—C005—C2—N1	-179.2 (12)		

Symmetry codes: (i) -x+3/2, -y+3/2, -z+1; (ii) x, -y+1, z+1/2; (iii) -x+3/2, y+1/2, -z+1/2; (iv) -x+1, y, -z+1/2; (v) -x+3/2, y-1/2, -z+1/2.

(1,3-XDA)PbBr$_4$

Br$_6$Pb·2(C$_8$H$_{14}$N$_2$)	$F(000)$ = 888
M_r = 963.07	D_x = 2.461 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 10.7571 (18) Å	Cell parameters from 463 reflections
b = 14.525 (3) Å	θ = 2.8–29.5°
c = 8.5545 (10) Å	μ = 15.73 mm^{-1}
β = 103.540 (4)°	T = 299 K

$V = 1299.4\ (4)\ \text{Å}^3$	Plate, clear light colourless
$Z = 2$	$0.1 \times 0.06 \times 0.02$ mm

Data collection

Bruker APEX-II CCD diffractometer	1816 independent reflections
Radiation source: microfocus sealed X-ray tube, Incoatec Iμs	1198 reflections with $I > 2\sigma(I)$
Mirror optics monochromator	$R_{int} = 0.138$
Detector resolution: 7.9 pixels mm^{-1}	$\theta_{max} = 23.1°$, $\theta_{min} = 2.4°$
ϕ and ω scans	$h = -11 \rightarrow 11$
Absorption correction: multi-scan	$k = -16 \rightarrow 16$
$T_{min} = 0.387$, $T_{max} = 0.746$	$l = -9 \rightarrow 9$
6279 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: dual
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.056$	H-atom parameters constrained
$wR(F^2) = 0.109$	$w = 1/[\sigma^2(F_o^2) + (0.0102P)^2 + 4.5929P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
1816 reflections	$\Delta\rangle_{max} = 1.03$ e Å^{-3}
126 parameters	$\Delta\rangle_{min} = -1.20$ e Å^{-3}
36 restraints	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
Pb01	0.000000	0.500000	0.500000	0.0298 (3)
Br02	0.05277 (19)	0.68916 (12)	0.3861 (2)	0.0387 (5)
Br03	0.1157 (2)	0.42698 (13)	0.2340 (2)	0.0425 (6)
Br04	0.24668 (19)	0.47621 (13)	0.7576 (2)	0.0421 (6)
N005	0.1922 (13)	0.6156 (9)	1.0435 (15)	0.033 (4)
H00A	0.203815	0.586873	0.956124	0.040*

H00B	0.155345	0.669941	1.015746	0.040*
H00C	0.142085	0.581580	1.089898	0.040*
N006	0.8163 (14)	0.7215 (9)	1.0566 (16)	0.038 (4)
H00D	0.878431	0.712810	1.005354	0.045*
H00E	0.812598	0.673304	1.119716	0.045*
H00F	0.832236	0.772211	1.116263	0.045*
C007	0.5784 (16)	0.7519 (12)	1.0059 (18)	0.027 (4)
C008	0.5540 (17)	0.8432 (12)	1.034 (2)	0.038 (5)
H008	0.606511	0.889824	1.011463	0.046*
C009	0.3760 (16)	0.7970 (12)	1.1373 (18)	0.029 (4)
H009	0.308952	0.813186	1.183351	0.035*
C00A	0.4500 (16)	0.8635 (12)	1.097 (2)	0.037 (5)
H00G	0.430365	0.924807	1.111167	0.044*
C00B	0.6907 (18)	0.7317 (14)	0.936 (2)	0.046 (6)
H00H	0.698636	0.780881	0.862224	0.055*
H00I	0.673575	0.675279	0.873887	0.055*
C00C	0.3986 (18)	0.7029 (14)	1.111 (2)	0.039 (5)
C00D	0.3210 (19)	0.6300 (13)	1.161 (2)	0.049 (6)
H00J	0.306632	0.645581	1.265722	0.059*
H00K	0.368576	0.572676	1.172210	0.059*
C00E	0.5056 (18)	0.6840 (13)	1.0481 (18)	0.038 (5)
H00L	0.527217	0.622934	1.034868	0.046*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb01	0.0334 (6)	0.0257 (6)	0.0317 (6)	0.0037 (5)	0.0107 (5)	0.0009 (5)
Br02	0.0383 (13)	0.0297 (11)	0.0467 (12)	-0.0019 (9)	0.0072 (10)	0.0007 (9)
Br03	0.0545 (15)	0.0329 (12)	0.0468 (12)	0.0059 (10)	0.0254 (11)	0.0001 (9)
Br04	0.0372 (13)	0.0406 (13)	0.0481 (12)	0.0001 (10)	0.0091 (10)	0.0054 (10)
N005	0.033 (10)	0.027 (9)	0.033 (9)	-0.004 (7)	-0.006 (8)	0.000 (7)
N006	0.046 (11)	0.032 (9)	0.038 (10)	0.007 (8)	0.014 (9)	-0.001 (7)
C007	0.023 (10)	0.035 (11)	0.021 (9)	-0.002 (9)	-0.002 (8)	-0.009 (8)
C008	0.027 (11)	0.040 (11)	0.049 (11)	-0.004 (9)	0.013 (9)	-0.014 (9)
C009	0.022 (11)	0.043 (11)	0.024 (10)	0.007 (9)	0.007 (8)	-0.007 (9)
C00A	0.016 (10)	0.030 (11)	0.053 (12)	0.013 (9)	-0.013 (9)	0.001 (9)
C00B	0.041 (14)	0.064 (15)	0.040 (12)	0.007 (12)	0.023 (11)	0.009 (11)
C00C	0.027 (11)	0.051 (12)	0.032 (11)	-0.014 (10)	-0.003 (9)	0.004 (9)
C00D	0.063 (17)	0.048 (14)	0.029 (12)	0.014 (12)	-0.002 (11)	0.008 (10)
C00E	0.045 (13)	0.041 (12)	0.027 (11)	0.002 (10)	0.008 (10)	-0.005 (9)

Geometric parameters (Å, °)

Pb01—Br02	3.0132 (19)	C007—C00B	1.50 (2)
Pb01—Br02[i]	3.0133 (19)	C007—C00E	1.36 (2)
Pb01—Br03	3.0298 (17)	C008—H008	0.9300
Pb01—Br03[i]	3.0298 (17)	C008—C00A	1.38 (2)
Pb01—Br04[i]	3.046 (2)	C009—H009	0.9300
Pb01—Br04	3.046 (2)	C009—C00A	1.35 (2)
N005—H00A	0.8900	C009—C00C	1.41 (2)
N005—H00B	0.8900	C00A—H00G	0.9300
N005—H00C	0.8900	C00B—H00H	0.9700
N005—C00D	1.52 (2)	C00B—H00I	0.9700
N006—H00D	0.8900	C00C—C00D	1.47 (2)
N006—H00E	0.8900	C00C—C00E	1.41 (2)
N006—H00F	0.8900	C00D—H00J	0.9700
N006—C00B	1.50 (2)	C00D—H00K	0.9700
C007—C008	1.38 (2)	C00E—H00L	0.9300
Br02—Pb01—Br02[i]	180.0	C00E—C007—C00B	122.1 (17)
Br02[i]—Pb01—Br03[i]	86.25 (5)	C007—C008—H008	120.8
Br02[i]—Pb01—Br03	93.75 (5)	C00A—C008—C007	118.4 (17)
Br02—Pb01—Br03[i]	93.75 (5)	C00A—C008—H008	120.8
Br02—Pb01—Br03	86.25 (5)	C00A—C009—H009	119.4
Br02[i]—Pb01—Br04[i]	98.00 (5)	C00A—C009—C00C	121.2 (16)
Br02[i]—Pb01—Br04	82.00 (5)	C00C—C009—H009	119.4
Br02—Pb01—Br04	98.00 (5)	C008—C00A—H00G	119.1
Br02—Pb01—Br04[i]	82.00 (5)	C009—C00A—C008	121.9 (17)
Br03[i]—Pb01—Br03	180.0	C009—C00A—H00G	119.1
Br03—Pb01—Br04	93.56 (5)	N006—C00B—H00H	108.5
Br03[i]—Pb01—Br04	86.44 (5)	N006—C00B—H00I	108.5
Br03—Pb01—Br04[i]	86.44 (5)	C007—C00B—N006	115.1 (13)
Br03[i]—Pb01—Br04[i]	93.56 (5)	C007—C00B—H00H	108.5
Br04[i]—Pb01—Br04	180.0	C007—C00B—H00I	108.5
H00A—N005—H00B	109.5	H00H—C00B—H00I	107.5
H00A—N005—H00C	109.5	C009—C00C—C00D	121.2 (17)
H00B—N005—H00C	109.5	C00E—C00C—C009	115.8 (16)
C00D—N005—H00A	109.5	C00E—C00C—C00D	122.7 (18)
C00D—N005—H00B	109.5	N005—C00D—H00J	108.9
C00D—N005—H00C	109.5	N005—C00D—H00K	108.9
H00D—N006—H00E	109.5	C00C—C00D—N005	113.4 (14)
H00D—N006—H00F	109.5	C00C—C00D—H00J	108.9
H00E—N006—H00F	109.5	C00C—C00D—H00K	108.9
C00B—N006—H00D	109.5	H00J—C00D—H00K	107.7

C00B—N006—H00E	109.5	C007—C00E—C00C	122.2 (17)
C00B—N006—H00F	109.5	C007—C00E—H00L	118.9
C008—C007—C00B	117.5 (16)	C00C—C00E—H00L	118.9
C00E—C007—C008	120.4 (16)		
C007—C008—C00A—C009	3 (3)	C00B—C007—C008—C00A	179.2 (16)
C008—C007—C00B—N006	87 (2)	C00B—C007—C00E—C00C	-178.8 (16)
C008—C007—C00E—C00C	4 (3)	C00C—C009—C00A—C008	-3 (3)
C009—C00C—C00D—N005	80 (2)	C00D—C00C—C00E—C007	-178.4 (17)
C009—C00C—C00E—C007	-4 (3)	C00E—C007—C008—C00A	-4 (3)
C00A—C009—C00C—C00D	177.6 (17)	C00E—C007—C00B—N006	-90 (2)
C00A—C009—C00C—C00E	3 (3)	C00E—C00C—C00D—N005	-105 (2)

Symmetry code: (i) -x, -y+1, -z+1.

(1,4-PDA)PbBr$_4$

Crystal data

$Br_4Pb \cdot C_6H_{10}N_2$	$Z = 2$
$M_r = 636.99$	$F(000) = 564$
Triclinic, $P\bar{1}$	$D_x = 3.211$ Mg m^{-3}
$a = 7.434$ (3) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 8.712$ (3) Å	Cell parameters from 2265 reflections
$c = 11.028$ (4) Å	$\theta = 3.6–27.0°$
$\alpha = 70.570$ (19)°	$\mu = 24.89$ mm^{-1}
$\beta = 78.527$ (19)°	$T = 302$ K
$\gamma = 89.414$ (19)°	Block, clear light white
$V = 658.9$ (4) Å^3	0.05 × 0.04 × 0.04 mm

Data collection

Bruker APEX-II CCD diffractometer	$R_{int} = 0.063$
Mirror optics monochromator	$\theta_{max} = 27.2°$, $\theta_{min} = 2.5°$
ϕ and ω scans	$h = -8 \rightarrow 8$
3512 measured reflections	$k = -11 \rightarrow 10$
2016 independent reflections	$l = -14 \rightarrow 13$

1244 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	48 restraints
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.065$	H-atom parameters constrained
$wR(F^2) = 0.171$	$w = 1/[\sigma^2(F_o^2) + (0.0667P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} < 0.001$
2016 reflections	$\Delta\rangle_{max} = 2.19$ e Å^{-3}
123 parameters	$\Delta\rangle_{min} = -2.24$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
Pb01	1.000000	1.000000	0.500000	0.0348 (4)
Pb02	0.500000	0.500000	0.500000	0.0341 (4)
Br03	0.1703 (4)	0.6986 (3)	0.4560 (3)	0.0451 (7)
Br04	1.0852 (4)	1.1549 (3)	0.2083 (2)	0.0442 (7)
Br05	0.3653 (4)	0.3594 (3)	0.7888 (2)	0.0453 (7)
Br06	0.6506 (4)	0.8083 (4)	0.5249 (3)	0.0580 (9)
N007	-0.057 (3)	0.470 (2)	0.7702 (18)	0.042 (5)
H00A	-0.074936	0.446191	0.700795	0.051*
H00B	0.061727	0.463052	0.773939	0.051*
H00C	-0.089793	0.570196	0.763079	0.051*
N008	-0.490 (3)	0.011 (2)	1.2266 (19)	0.049 (6)
H00D	-0.496101	-0.085757	1.216269	0.059*
H00E	-0.601774	0.047215	1.238424	0.059*
H00F	-0.441572	0.001027	1.296478	0.059*
C009	-0.371 (3)	0.128 (2)	1.108 (2)	0.025 (4)
C00A	-0.161 (4)	0.196 (3)	0.904 (2)	0.041 (6)
H00G	-0.087370	0.163463	0.839312	0.049*
C00B	-0.263 (4)	0.081 (3)	1.012 (2)	0.047 (6)
H00H	-0.259684	-0.029020	1.019908	0.056*
C00C	-0.165 (3)	0.356 (3)	0.888 (2)	0.034 (5)

C00D	-0.377 (3)	0.292 (3)	1.098 (2)	0.042 (6)
H00I	-0.447554	0.324872	1.162959	0.051*
C00E	-0.274 (3)	0.400 (3)	0.988 (2)	0.037 (5)
H00J	-0.275976	0.510334	0.979438	0.045*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb01	0.0365 (9)	0.0292 (7)	0.0364 (8)	-0.0007 (6)	-0.0024 (6)	-0.0108 (6)
Pb02	0.0365 (9)	0.0290 (7)	0.0349 (8)	0.0021 (6)	-0.0047 (6)	-0.0099 (6)
Br03	0.0417 (16)	0.0431 (15)	0.0499 (16)	0.0116 (12)	-0.0075 (12)	-0.0163 (12)
Br04	0.0609 (19)	0.0326 (13)	0.0396 (15)	0.0069 (13)	-0.0105 (13)	-0.0130 (11)
Br05	0.0597 (19)	0.0356 (14)	0.0367 (15)	0.0045 (13)	-0.0031 (13)	-0.0113 (11)
Br06	0.0499 (19)	0.0656 (19)	0.064 (2)	-0.0105 (15)	-0.0107 (15)	-0.0285 (15)
N007	0.046 (14)	0.028 (11)	0.042 (13)	0.004 (10)	0.006 (10)	-0.007 (9)
N008	0.053 (15)	0.030 (12)	0.050 (14)	-0.007 (11)	0.005 (11)	-0.003 (10)
C009	0.022 (12)	0.029 (9)	0.024 (10)	0.013 (9)	-0.018 (8)	-0.002 (8)
C00A	0.068 (16)	0.025 (9)	0.029 (11)	0.006 (11)	-0.005 (9)	-0.012 (8)
C00B	0.063 (16)	0.031 (10)	0.038 (13)	0.013 (11)	0.005 (10)	-0.009 (8)
C00C	0.030 (13)	0.029 (8)	0.045 (12)	0.001 (10)	-0.001 (9)	-0.020 (9)
C00D	0.031 (14)	0.036 (10)	0.056 (13)	0.004 (11)	0.006 (10)	-0.018 (10)
C00E	0.032 (13)	0.032 (10)	0.050 (13)	0.005 (10)	-0.001 (9)	-0.021 (8)

Geometric parameters (Å, °)

Pb01—Br03[i]	3.045 (3)	N007—C00C	1.43 (3)
Pb01—Br03[ii]	3.045 (3)	N008—H00D	0.8900
Pb01—Br04[iii]	2.982 (3)	N008—H00E	0.8900
Pb01—Br04	2.982 (3)	N008—H00F	0.8900
Pb01—Br06[iii]	3.018 (3)	N008—C009	1.48 (3)
Pb01—Br06	3.018 (3)	C009—C00B	1.37 (3)
Pb02—Br03[iv]	3.010 (3)	C009—C00D	1.39 (3)
Pb02—Br03	3.010 (3)	C00A—H00G	0.9300
Pb02—Br05[iv]	2.968 (3)	C00A—C00B	1.37 (3)
Pb02—Br05	2.968 (3)	C00A—C00C	1.34 (3)
Pb02—Br06[iv]	3.037 (3)	C00B—H00H	0.9300
Pb02—Br06	3.037 (3)	C00C—C00E	1.40 (3)
N007—H00A	0.8900	C00D—H00I	0.9300
N007—H00B	0.8900	C00D—C00E	1.35 (3)
N007—H00C	0.8900	C00E—H00J	0.9300
Br03[ii]—Pb01—Br03[i]	180.0	Pb01—Br06—Pb02	143.81 (12)

Br04—Pb01—Br03[ii]	93.41 (7)	H00A—N007—H00B	109.5
Br04[iii]—Pb01—Br03[i]	93.41 (7)	H00A—N007—H00C	109.5
Br04—Pb01—Br03[i]	86.59 (7)	H00B—N007—H00C	109.5
Br04[iii]—Pb01—Br03[ii]	86.59 (7)	C00C—N007—H00A	109.5
Br04—Pb01—Br04[iii]	180.0	C00C—N007—H00B	109.5
Br04—Pb01—Br06[iii]	82.19 (8)	C00C—N007—H00C	109.5
Br04—Pb01—Br06	97.81 (8)	H00D—N008—H00E	109.5
Br04[iii]—Pb01—Br06	82.19 (8)	H00D—N008—H00F	109.5
Br04[iii]—Pb01—Br06[iii]	97.81 (8)	H00E—N008—H00F	109.5
Br06[iii]—Pb01—Br03[i]	98.51 (8)	C009—N008—H00D	109.5
Br06—Pb01—Br03[ii]	98.51 (8)	C009—N008—H00E	109.5
Br06[iii]—Pb01—Br03[ii]	81.49 (8)	C009—N008—H00F	109.5
Br06—Pb01—Br03[i]	81.49 (8)	C00B—C009—N008	122.8 (19)
Br06—Pb01—Br06[iii]	180.0	C00B—C009—C00D	121 (2)
Br03—Pb02—Br03[iv]	180.0	C00D—C009—N008	116 (2)
Br03—Pb02—Br06	82.42 (8)	C00B—C00A—H00G	119.0
Br03—Pb02—Br06[iv]	97.58 (8)	C00C—C00A—H00G	119.0
Br03[iv]—Pb02—Br06	97.58 (8)	C00C—C00A—C00B	122 (2)
Br03[iv]—Pb02—Br06[iv]	82.42 (8)	C009—C00B—H00H	120.3
Br05—Pb02—Br03	94.00 (8)	C00A—C00B—C009	119 (2)
Br05—Pb02—Br03[iv]	86.00 (8)	C00A—C00B—H00H	120.3
Br05[iv]—Pb02—Br03	86.00 (8)	C00A—C00C—N007	119 (2)
Br05[iv]—Pb02—Br03[iv]	94.00 (8)	C00A—C00C—C00E	117 (2)
Br05—Pb02—Br05[iv]	180.00 (11)	C00E—C00C—N007	124 (2)
Br05—Pb02—Br06	91.20 (8)	C009—C00D—H00I	121.5
Br05—Pb02—Br06[iv]	88.80 (8)	C00E—C00D—C009	117 (2)
Br05[iv]—Pb02—Br06	88.80 (8)	C00E—C00D—H00I	121.5
Br05[iv]—Pb02—Br06[iv]	91.20 (8)	C00C—C00E—H00J	118.3
Br06[iv]—Pb02—Br06	180.0	C00D—C00E—C00C	123 (2)
Pb02—Br03—Pb01[v]	140.42 (10)	C00D—C00E—H00J	118.3
N007—C00C—C00E—C00D	179 (2)	C00B—C009—C00D—C00E	1 (4)
N008—C009—C00B—C00A	179 (2)	C00B—C00A—C00C—N007	-179 (2)
N008—C009—C00D—C00E	-178 (2)	C00B—C00A—C00C—C00E	2 (4)
C009—C00D—C00E—C00C	0 (4)	C00C—C00A—C00B—C009	-1 (4)
C00A—C00C—C00E—C00D	-1 (4)	C00D—C009—C00B—C00A	-1 (4)

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) -*x*+1, -*y*+2, -*z*+1; (iii) -*x*+2, -*y*+2, -*z*+1; (iv) -*x*+1, -*y*+1, -*z*+1; (v) *x*-1, *y*,

z.

(1,4-XDA)PbBr$_4$

Br$_4$Pb·C$_8$H$_{14}$N$_2$	$F(000) = 596$
$M_r = 665.04$	$D_x = 2.688$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 12.3274$ (7) Å	Cell parameters from 7438 reflections
$b = 8.1618$ (4) Å	$\theta = 3.0–32.0°$
$c = 8.1675$ (4) Å	$\mu = 19.97$ mm^{-1}
$\beta = 90.817$ (2)°	$T = 299$ K
$V = 821.68$ (7) Å^3	Plate, clear light yellow
$Z = 2$	$0.1 \times 0.06 \times 0.04$ mm

Data collection

Bruker SMART APEX2 area detector diffractometer	3501 independent reflections
Radiation source: microfocus sealed X-ray tube, Incoatec Iµs	2198 reflections with $I > 2\sigma(I)$
Mirror optics monochromator	$R_{int} = 0.048$
Detector resolution: 7.9 pixels mm^{-1}	$\theta_{max} = 35.0°$, $\theta_{min} = 3.0°$
ω and ϕ scans	$h = -17 \rightarrow 19$
Absorption correction: multi-scan *SADABS2016*/2 (Bruker,2016/2) was used for absorption correction. wR2(int) was 0.1002 before and 0.0515 after correction. The Ratio of minimum to maximum transmission is 0.5817. The $\lambda/2$ correction factor is Not present.	$k = -9 \rightarrow 12$
$T_{min} = 0.435$, $T_{max} = 0.747$	$l = -13 \rightarrow 13$
9093 measured reflections	

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.053$	H-atom parameters constrained
$wR(F^2) = 0.123$	$w = 1/[\sigma^2(F_o^2) + 10.2448P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} < 0.001$
3501 reflections	$\Delta\rangle_{max} = 1.58$ e Å^{-3}
71 parameters	$\Delta\rangle_{min} = -1.86$ e Å^{-3}

Special details

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{iso}*/U_{eq}$
Pb01	0.500000	1.000000	0.500000	0.02888 (12)
N1	0.2886 (6)	0.5754 (10)	0.5727 (11)	0.0462 (19)
H1A	0.270996	0.677669	0.545463	0.055*
H1B	0.359728	0.561273	0.561607	0.055*
H1C	0.270681	0.556929	0.676247	0.055*
C3	0.0566 (9)	0.3954 (18)	0.5982 (18)	0.075 (4)
H3	0.093815	0.324965	0.668631	0.089*
Br02	0.50046 (8)	0.81675 (11)	0.81624 (11)	0.0422 (2)
C1	0.2308 (10)	0.4621 (16)	0.4667 (17)	0.067 (3)
H1D	0.252649	0.350927	0.493306	0.080*
H1E	0.249968	0.483141	0.353830	0.080*
Br03	0.25637 (8)	0.97823 (13)	0.48251 (13)	0.0482 (2)
C2	0.1107 (7)	0.4778 (12)	0.4843 (13)	0.046 (2)
C4	0.0543 (10)	0.586 (2)	0.3877 (18)	0.082 (5)
H4	0.091255	0.648719	0.311316	0.099*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb01	0.0345 (2)	0.02755 (18)	0.02462 (18)	-0.00147 (18)	0.00016 (13)	-0.00003 (16)
N1	0.037 (4)	0.044 (4)	0.057 (5)	0.000 (4)	-0.001 (4)	0.004 (4)
C3	0.029 (5)	0.098 (10)	0.097 (10)	0.009 (6)	-0.001 (6)	0.049 (8)
Br02	0.0517 (5)	0.0397 (4)	0.0351 (4)	-0.0047 (4)	0.0001 (4)	0.0128 (4)
C1	0.052 (7)	0.071 (8)	0.077 (9)	-0.004 (6)	-0.004 (6)	-0.004 (6)
Br03	0.0380 (5)	0.0514 (6)	0.0552 (6)	0.0028 (4)	0.0019 (4)	0.0022 (4)
C2	0.031 (5)	0.051 (6)	0.056 (6)	0.000 (4)	-0.005 (4)	-0.005 (5)
C4	0.052 (7)	0.107 (11)	0.088 (10)	-0.007 (7)	-0.002 (7)	0.046 (9)

Geometric parameters (Å, °)

Pb01—Br02[i]	2.9846 (8)	N1—C1	1.448 (14)
Pb01—Br02[ii]	2.9894 (8)	C3—H3	0.9300
Pb01—Br02	2.9846 (8)	C3—C2	1.334 (15)
Pb01—Br02[iii]	2.9894 (8)	C3—C4[iv]	1.381 (17)
Pb01—Br03[i]	3.0099 (10)	C1—H1D	0.9700

Pb01—Br03	3.0099 (10)	C1—H1E	0.9700
N1—H1A	0.8900	C1—C2	1.495 (15)
N1—H1B	0.8900	C2—C4	1.369 (16)
N1—H1C	0.8900	C4—H4	0.9300
Br02^i—Pb01—Br02	180.0	C1—N1—H1B	109.5
Br02—Pb01—Br02^{iii}	89.936 (9)	C1—N1—H1C	109.5
Br02^i—Pb01—Br02^{iii}	90.064 (9)	C2—C3—H3	119.7
Br02^i—Pb01—Br02^{ii}	89.936 (9)	C2—C3—C4^{iv}	120.6 (11)
Br02—Pb01—Br02^{ii}	90.064 (9)	C4^{iv}—C3—H3	119.7
Br02^{ii}—Pb01—Br02^{iii}	180.0	Pb01—Br02—Pb01^v	150.21 (4)
Br02^{iii}—Pb01—Br03	93.78 (3)	N1—C1—H1D	109.3
Br02—Pb01—Br03	90.06 (3)	N1—C1—H1E	109.3
Br02^i—Pb01—Br03	89.94 (3)	N1—C1—C2	111.5 (10)
Br02—Pb01—Br03^i	89.94 (3)	H1D—C1—H1E	108.0
Br02^{ii}—Pb01—Br03	86.22 (3)	C2—C1—H1D	109.3
Br02^{ii}—Pb01—Br03^i	93.78 (3)	C2—C1—H1E	109.3
Br02^i—Pb01—Br03^i	90.06 (3)	C3—C2—C1	122.0 (10)
Br02^{iii}—Pb01—Br03^i	86.22 (3)	C3—C2—C4	118.2 (10)
Br03^i—Pb01—Br03	180.0	C4—C2—C1	119.7 (11)
H1A—N1—H1B	109.5	C3^{iv}—C4—H4	119.4
H1A—N1—H1C	109.5	C2—C4—C3^{iv}	121.1 (12)
H1B—N1—H1C	109.5	C2—C4—H4	119.4
C1—N1—H1A	109.5		
N1—C1—C2—C3	-86.9 (15)	C1—C2—C4—C3^{iv}	-179.5 (13)
N1—C1—C2—C4	89.4 (15)	C4^{iv}—C3—C2—C1	179.4 (13)
C3—C2—C4—C3^{iv}	-3 (3)	C4^{iv}—C3—C2—C4	3 (3)

Symmetry codes: (i) -x+1, -y+2, -z+1; (ii) x, -y+3/2, z-1/2; (iii) -x+1, y+1/2, -z+3/2; (iv) -x, -y+1, -z+1; (v) -x+1, y-1/2, -z+3/2.

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