

Supporting Information

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Synthesis, characterization and optoelectronic properties of 2D
hybrid RPbX_4 semiconductors based on an isomer mixture of
hexanedi-amine-based dications

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The here reported 2D iodine-based compound formed crystals with unusually low PL intensity and broad excitonic absorption peaks, when compared to the usual 2D lead iodine hybrid organic inorganic semiconductors, e.g. (Phe)₂PbI₄. Thus, in order to check its properties' relation to the synthetic procedure, **m1** variants were synthesized, information collected in Table 1. Other efforts where Pb was introduced in the form of oxides/salts provided inconclusive results; All variants have the required amount of HI to protonate the amine, with **m1_ns3/ns4** having double amount; **m1** and **m1_ns2** have less than required Pb content with regard to to the amine content, while **m1_ns3/ns4** have more than double needed HI and slightly more Pb content than the amine. It appears that **m1** and **m1_ns2** which have more organic component than the ideally required to form 2D semiconductor exhibit the well known excitonic peaks at ca. 500 nm and slightly Stokes-shifted PL peaks, where the **m1_ns3/ns4** samples, which contained more PbI₂, giving rise to defects as seen from the more shifted PL peaks and the lack of strong/sharp excitonic peaks at room temperature.

Table 1. All quantities values are in mmol expect for acetonitrile (AcN) which is in mL. R:Pb:I notes the starting molar ratio in the solution, without accounting the solubility of each possible component in the final solution after precipitation; ideally this would be 1:1:4.

	Organic precursor solution				Inorganic precursor solution				
Sample	Organic component	HI	AcN		PbI ₂	HI	AcN	T	R:Pb:I
m1	1.3	2.2	-	<i>mixed with →</i>	1	0.456	1.2	40°C	1:0.75:3.6
m1_ns2	1.2	-	-	<i>added to →</i>	0.6	2.28	6.5	40°C	1:0.50:2.9
m1_ns3	0.66	-	-	<i>mixed with →</i>	0.71	2.68	5	40°C	1:1.07:6.2
m1_ns4	0.45	1	2	<i>mixed with →</i>	0.5	1	2	80°C	1:1.11:6.8

Synthesis of **m1_ns2**

0.28 g of PbI_2 (0.6 mmol) were dissolved in 6.5 mL of acetonitrile, followed by the addition of 300 μL of 57% aqueous hydroiodic acid (2.28 mmol). By adding 111 μL of 2,2,4(2,4,4)-trimethyl-1,6-hexanediamine (0.6 mmol), fast precipitation of an orange-yellow solid occurred, while a second addition of 120 μL of amine (0.66 mmol) further forced an extra layer of precipitate. The solid was separated and washed rapidly with acetonitrile. Its color changes upon drying at low temperatures, yet this presents weak visual luminescence when excited with a 400 nm laser, not as strong as that observed from the standard 2D HOIS materials, such as those based on phenethylamine for example. In Figure S1, the powder XRD pattern is provided where an intense peak at ca. 6.89° is observed, different to that of **m1**. SEM images (Fig. S2) shows the existence of a needle-like microstructure incorporated in the flower-like structure. According to the optical absorption (OA) spectra (Fig. S3) and PL spectra (Fig. S4), the excitonic peak is observed at 487 nm which is at smaller wavelengths than for **m1**, presumably due to some sort of quantum confinement induced by the much less available amount of Pb. On the other hand, despite the 487 nm, only the ca. 530 nm peak of **m1** appears in the PL spectra of **m1_ns2** with ca. 50 nm FWHM and there is no peak close to the 487 nm value.

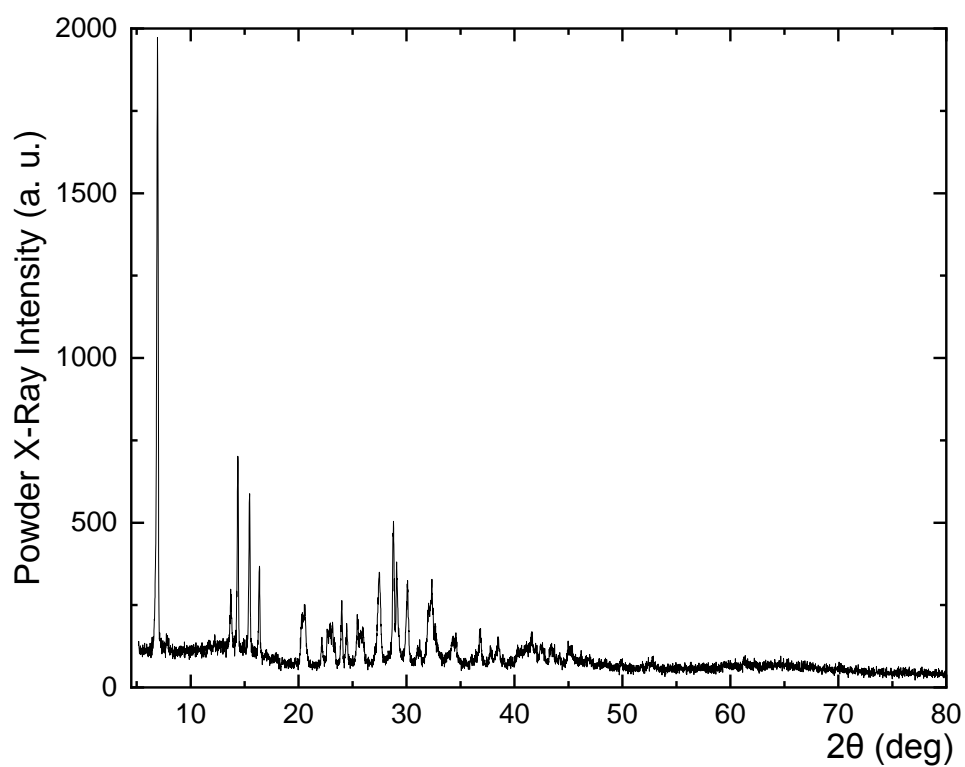


Figure S1. Powder XRD pattern for **m1_ns2**.

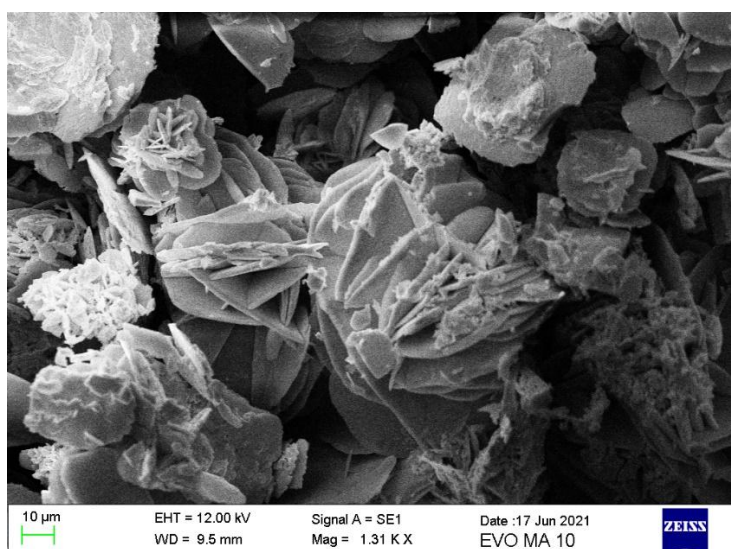
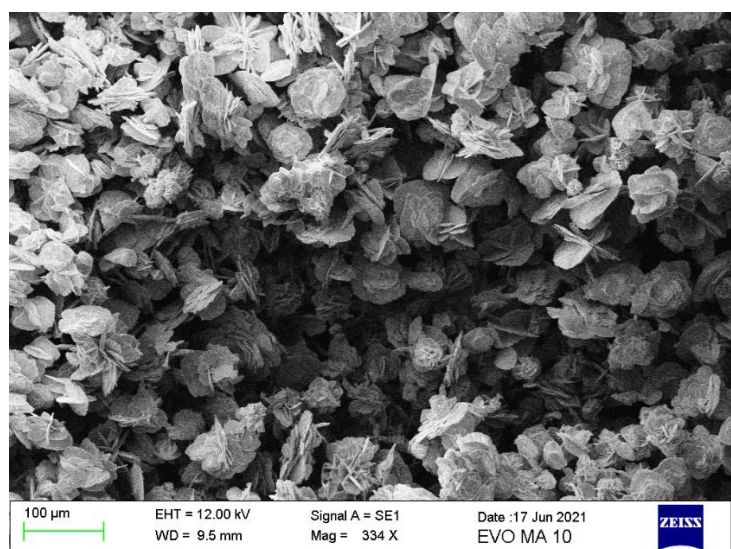


Figure S2. SEM images for **m1_ns2**.

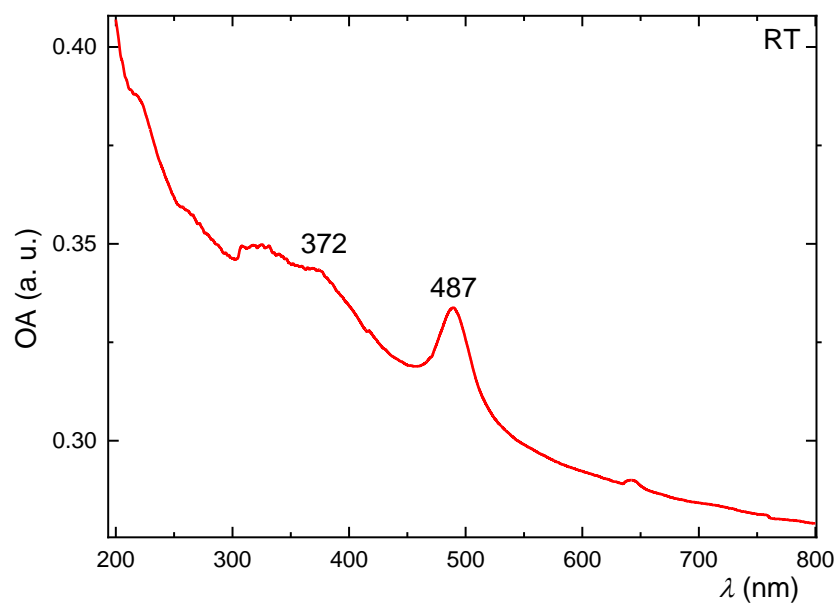


Figure S3. UV/Vis OA spectra for **m1_ns2**.

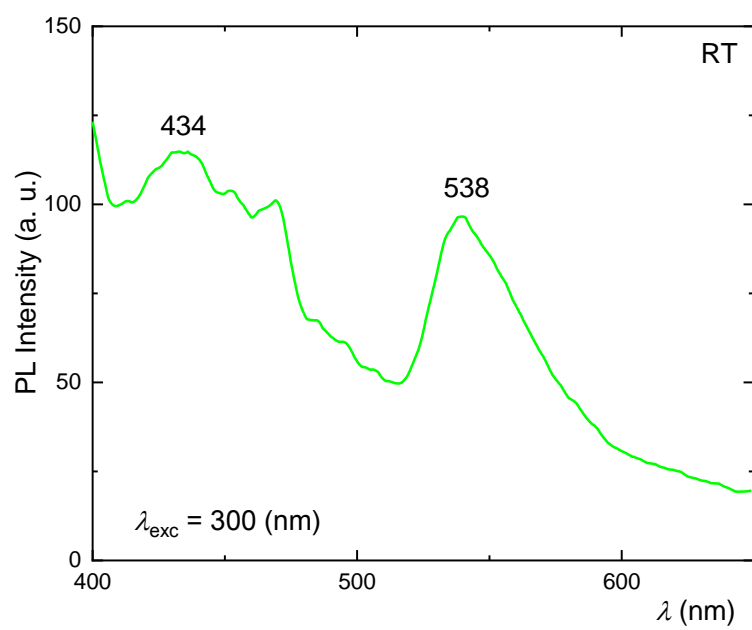


Figure S4. PL spectra for **m1_ns2**.

Synthesis of **m1_ns3**

0.33 g of PbI_2 (0.71 mmol) was dissolved in 5 mL of acetonitrile, followed by the addition of 360 μL of 57% aqueous hydroiodic acid (2.6 mmol). Upon addition of 120 μL of 2,2,4(2,4,4)-trimethyl-1,6-hexanediamine (0.66 mmol), an orange-yellow solid precipitated. This was separated and washed rapidly with acetonitrile under vacuum filtration. The dissolved perovskite nanoparticles, which remained within the supernatant solution, also gave rise to stronger green PL, which was centered at 540 nm. In the XRPD pattern (Fig. S5), double peaks at 6.89° and 7.55° at low angles are observed, implying that the 2D structure could form with some altered space group than that of the **m1** or **m1_ns2**. According to the SEM images (Fig. S6), the compound appears to have the same microstructure as **m1_ns2**, yet different XRPD pattern. The optoelectronic properties according to the optical absorption (OA) spectra (Fig. S7) present a peak at 363 nm. It is also interesting that there is a very weak peak at the 2D exciton's expected position of ca. 500-510 nm, i.e. here at 506 nm, yet there is an associated PL peak due to defects 547 nm (Fig. S8).

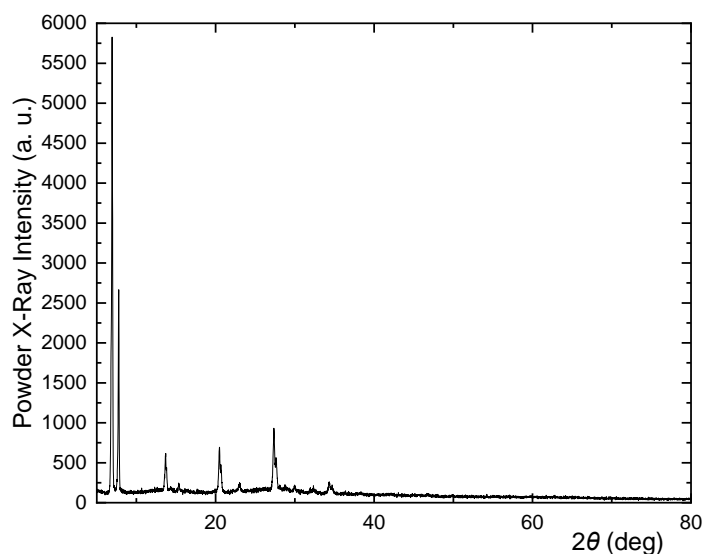


Figure S5. Powder XRD pattern for **m1_ns3**.

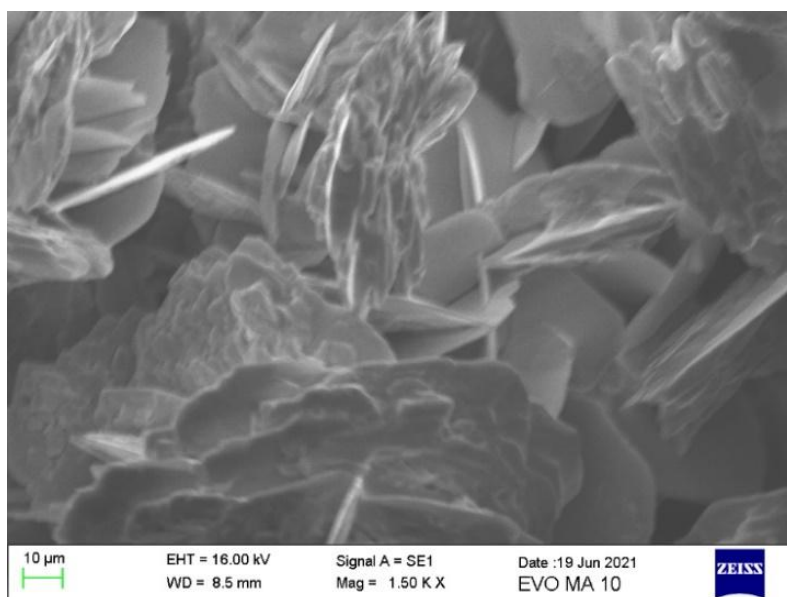


Figure S6. SEM image of **m1_ns3**.

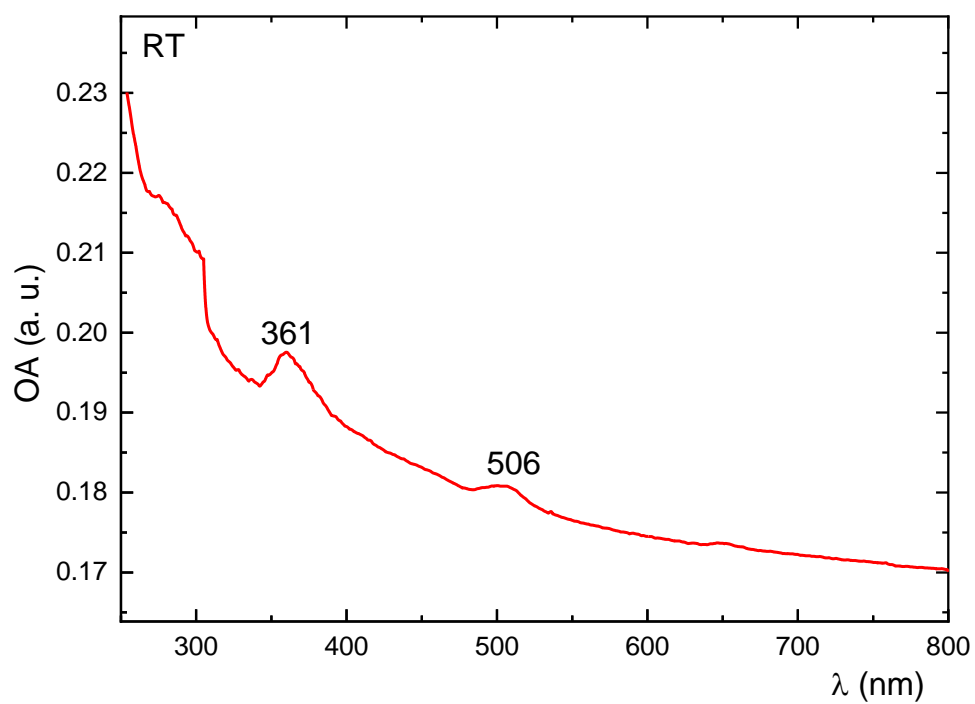


Figure S7. UV/VIS OA spectra for **m1_ns3**.

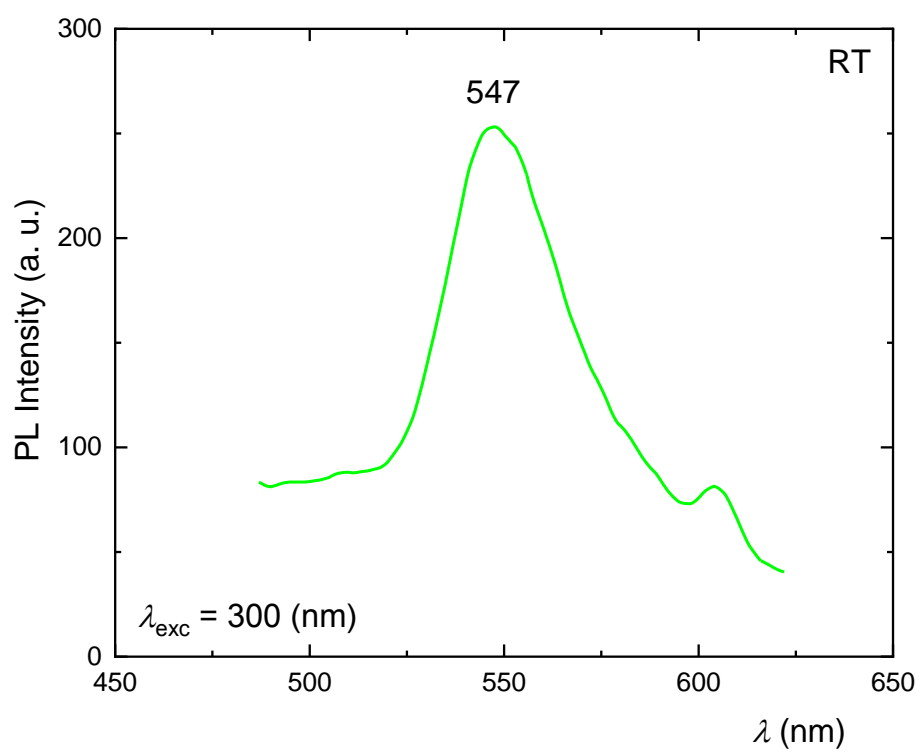


Figure S8. PL spectra for **m1_ns3**.

Synthesis of m1_ns4

0.24 g of PbI_2 (0.5 mmol) was dissolved in 2 mL acetonitrile at 60 °C with 136 μL 57% aqueous HI (1 mmol), until the solution appeared transparent yellowish. Separately, 82 mg of 2,2,4(2,4,4)-trimethyl-1,6-hexanediamine (0.45 mmol) were mixed with 136 μL 57% aqueous hydroiodic acid (1 mmol) under stirring at room temperature. The two aforementioned solutions were mixed and immediately formed a yellow precipitate as well as a green-luminescent yellow-orange solution. In the next minutes that the solution remained as so, its precipitate's luminescence dropped as it was monitored with a 405 nm 5mW laser, while the PL of the material dried on the beaker wall was intact. The supernatant unreacted liquid was removed and the precipitate was left to dry under vacuum; the supernatant was also left to dry under vacuum which contained most of the unreacted HI. According to the XRPD pattern (Fig. S9), sharp low angle peaks centered at ca. 6.87 ° and ca. 7.86°, due to the created lamellar structure. The double peaks imply that there are again as in **m1_ns2** two variants, however, the broadness of the second shows that it is due to lack of extra amine. The remaining high angle observed XRD peaks do not correspond to any known inorganic lead iodide containing structure. Due to its morphology, it was impractical to obtain a high-resolution SEM image other than images as in Fig. S10. The optical absorption (OA) spectra show an excitonic peak at 502 nm while the PL spectra with various excitation wavelengths, such as 350 and 450 nm, show a peak at 542 nm (Fig. S12) while the synchronous revealed peaks at 368, 498 and 548 nm (Fig. S12). The peak at ca. 502 nm is related to the 2D exciton, while the band at 548 nm is related to defects. The synchronous scan, which is closely related to the OA spectra, reveals the excitonic peak at slight blue shifted position of 498 nm, while it also reveals the low lying 548 nm band.

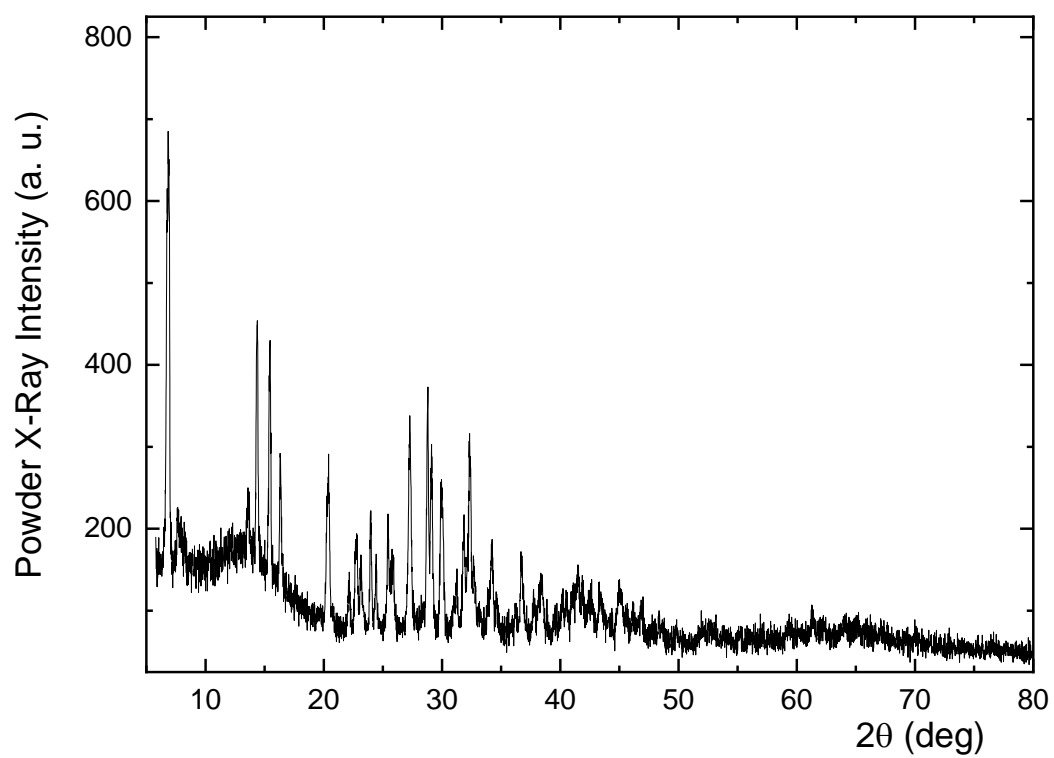


Figure S9. Powder XRD pattern for **m1_ns4**.

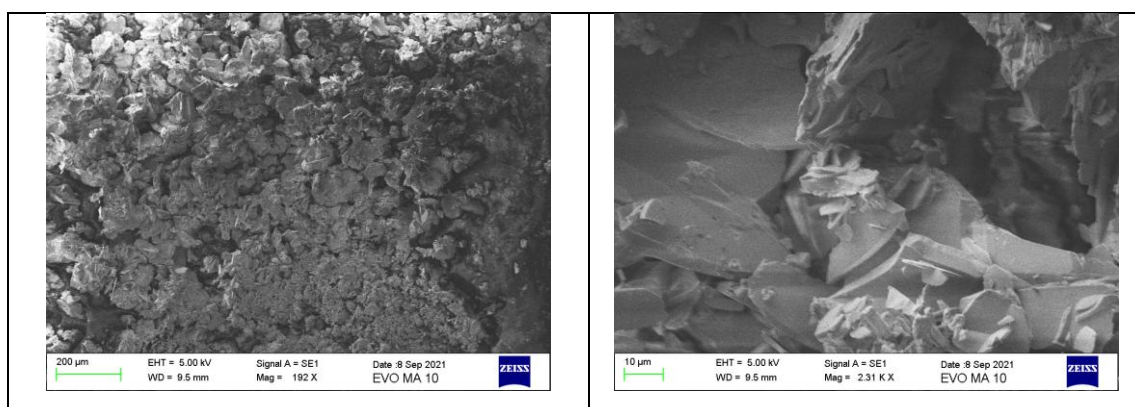


Figure S10. SEM image for **m1_ns4**.

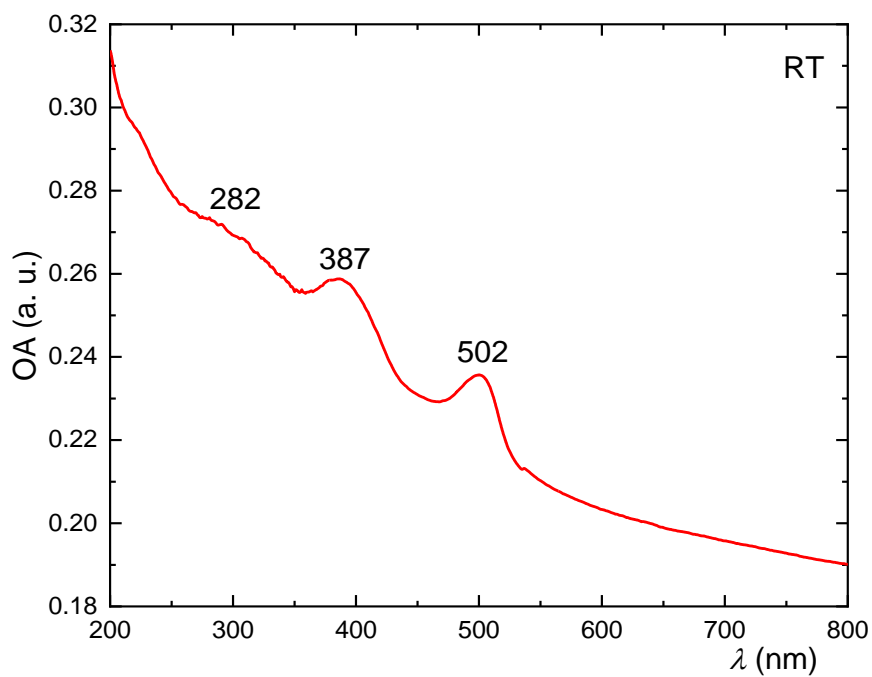


Figure S11. UV/Vis OA spectra for **m1_ns4** as prepared.

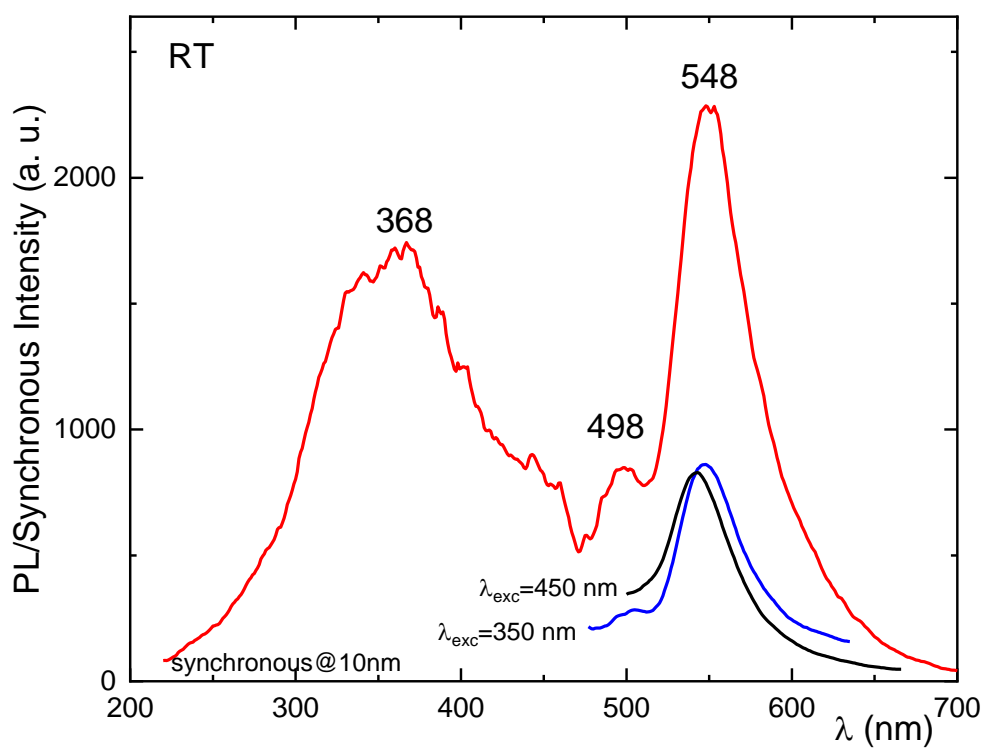


Figure S12. PL spectra for **m1_ns4** with $\lambda_{\text{exc}} = 350$ and 450 nm and synchronous scan set with slits at 2.5 nm and $\lambda_{\text{em}} - \lambda_{\text{exc}} = 10$ nm. No strong PLE signal was recorded.

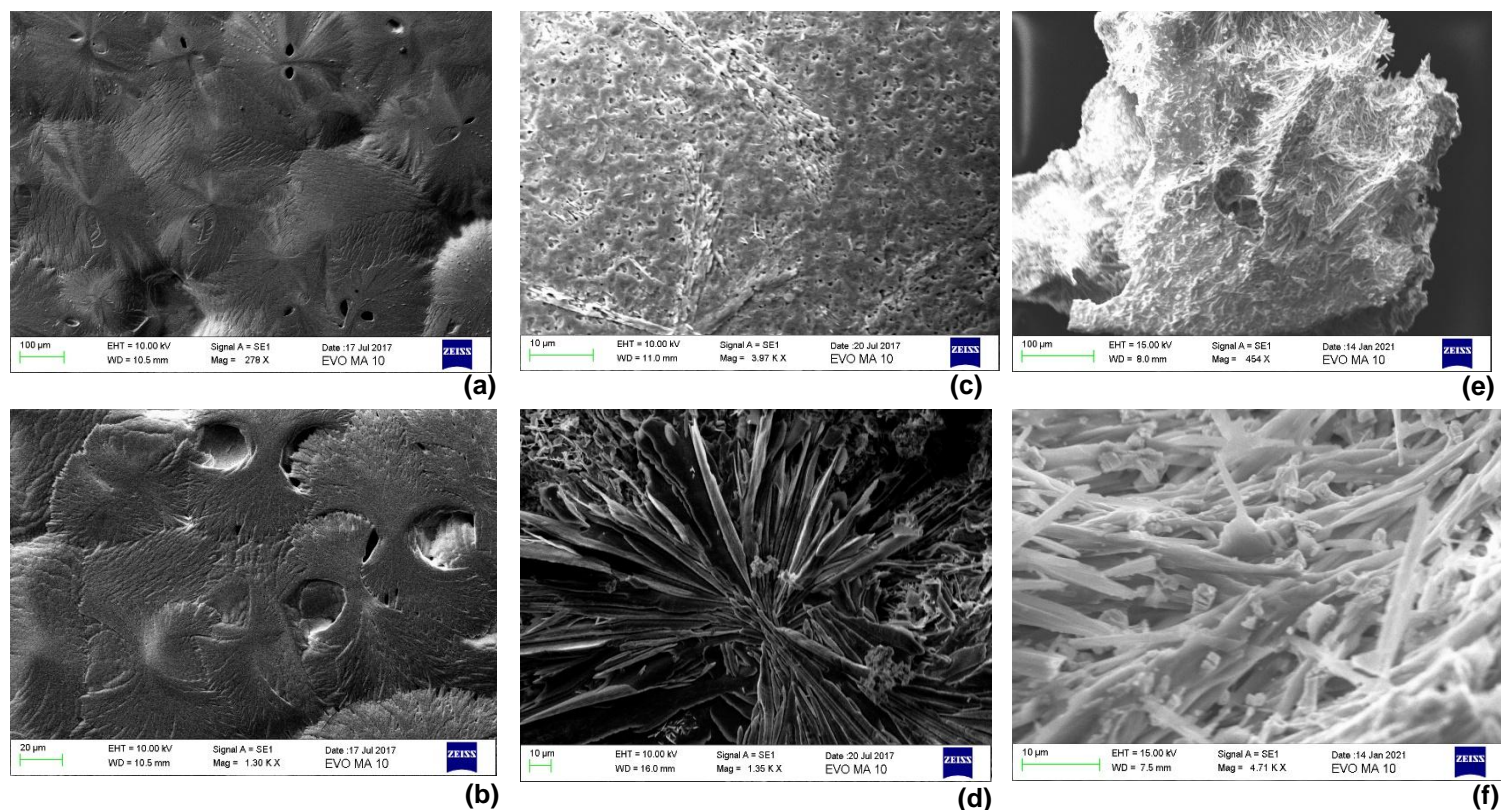


Figure S13. SEM images of compounds **m1** (a–b), **m2** (c–d) and **m3** (e–f).

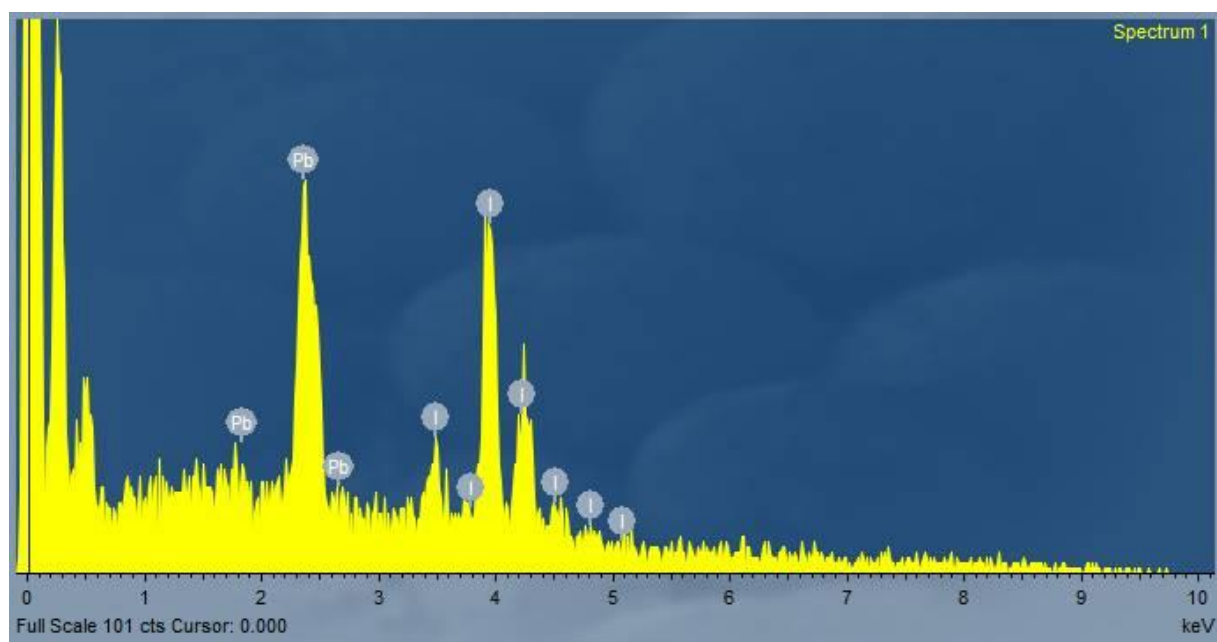


Figure S14. EDX spectra of **m1**.

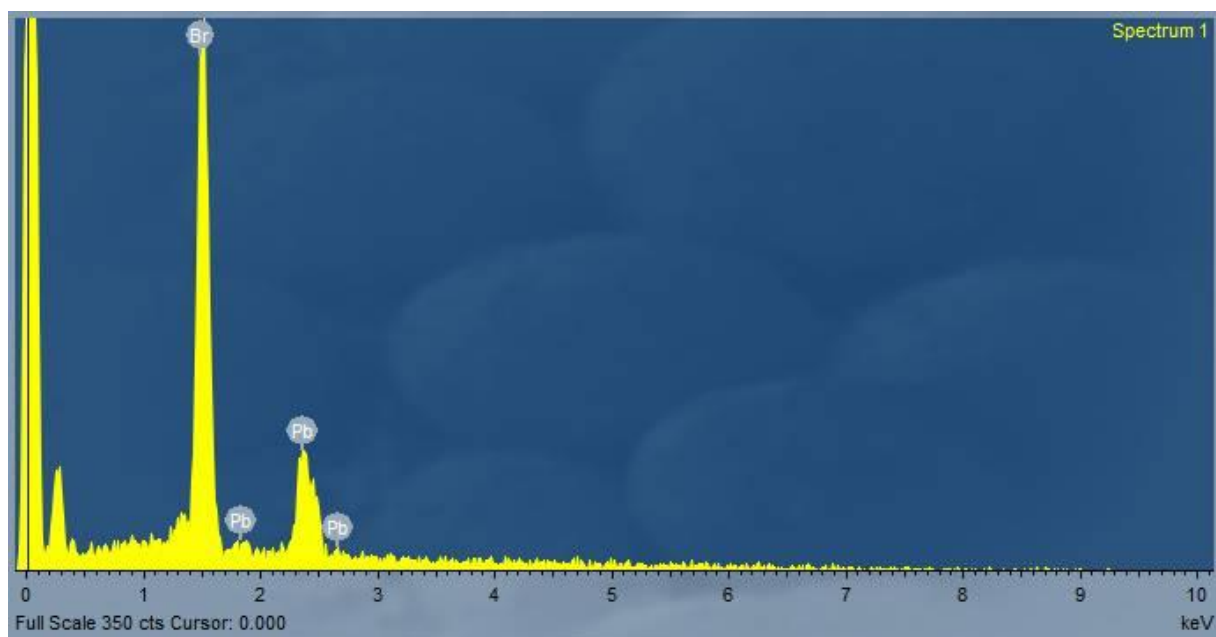


Figure S15. EDX spectra of **m2**.

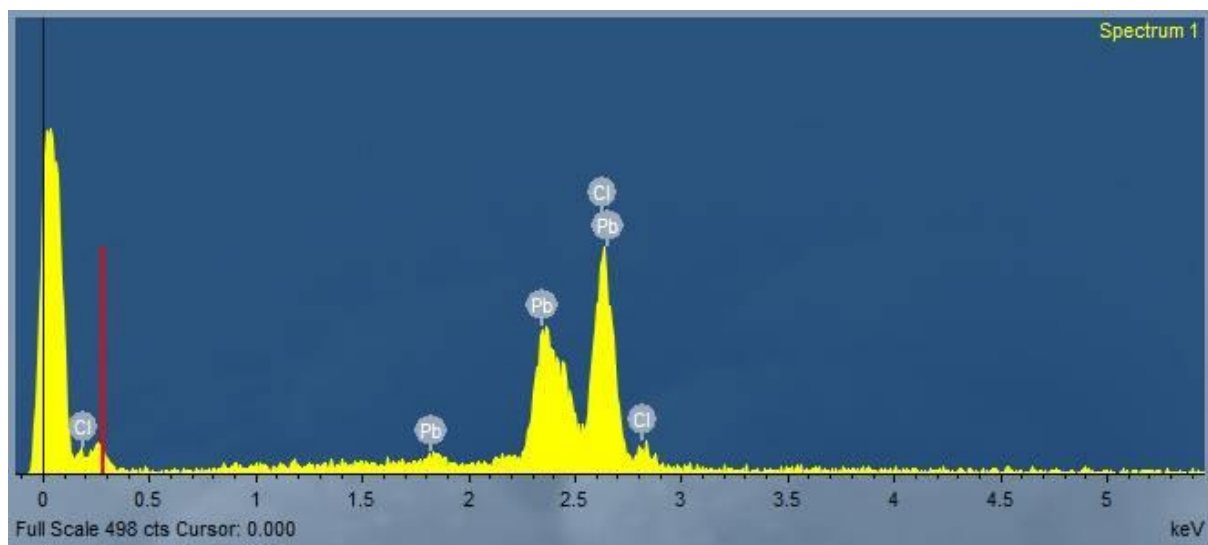


Figure S16. EDX spectra of **m3**.

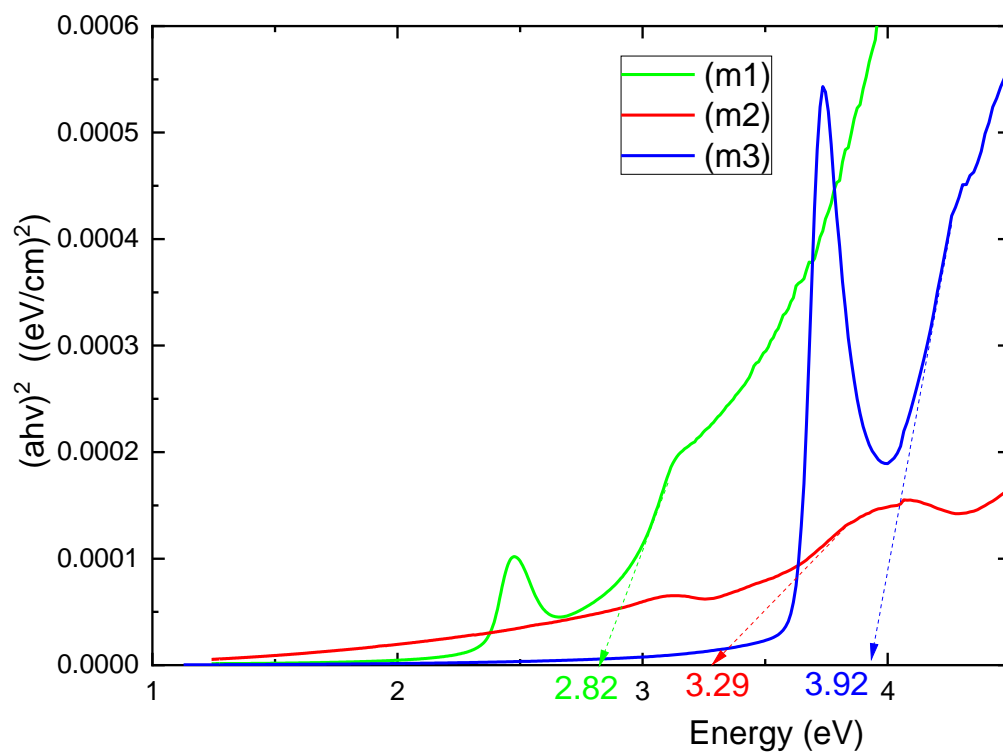


Figure S17. Tauc plots for compounds **m1** (green), **m2** (red) and **m3** (blue).

Amine Molecular Conformation

Optimization of the 2,2,4 isomer using the DMOL3 package (DN basis, GGA, BLYP). From left to right, neutral amine, amine with +2 charge due to extra 2 hydrogens added to the N atoms (double protonated), amine with two HI molecules.

Table 2. Ab initio geometry optimization of 2,2,4

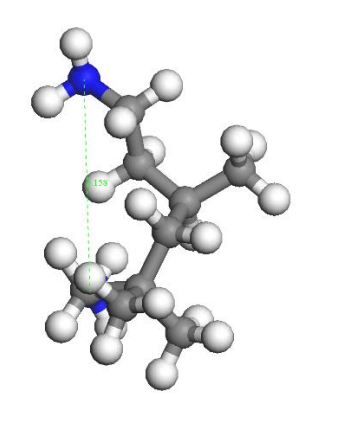
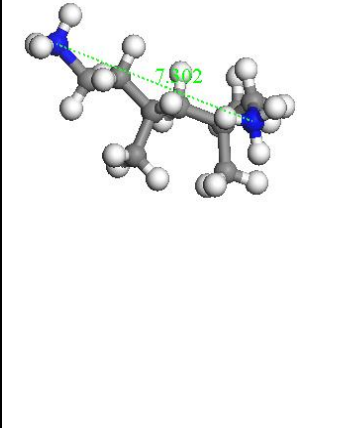
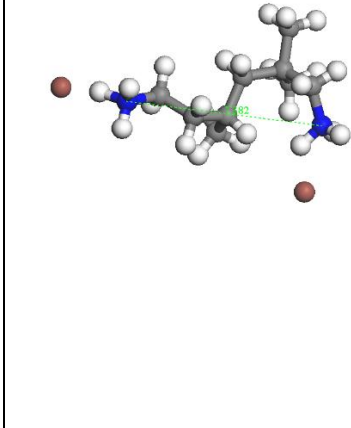
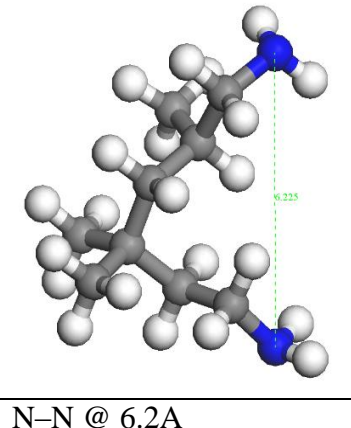
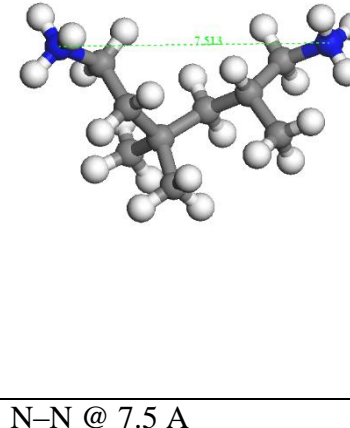
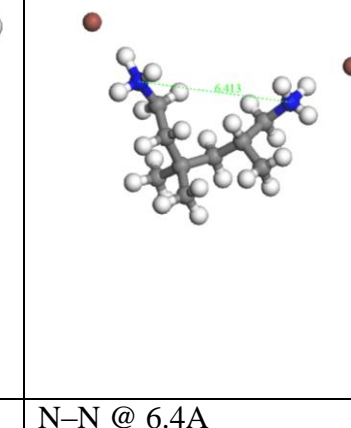
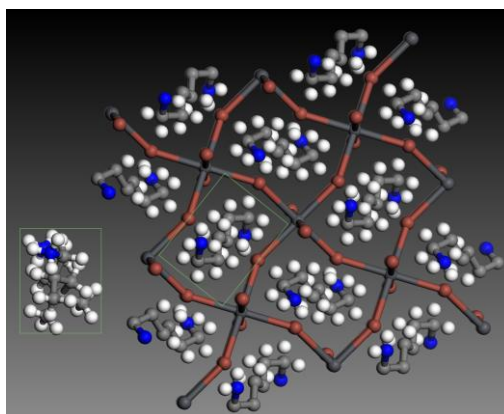
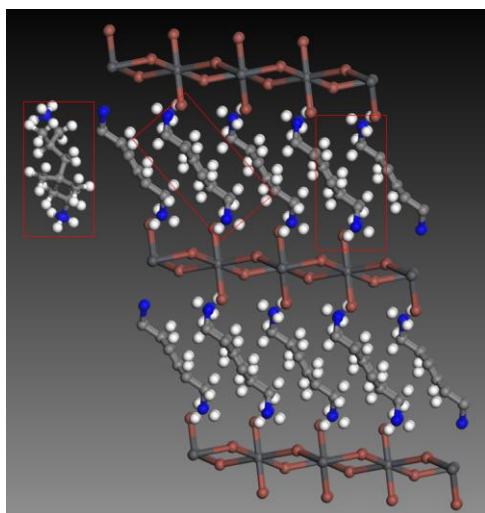
		
N-N @ 5.16A	N-N @ 7.3A	N-N @ 7.3A

Table 3. Ab initio geometry optimization of 2,4,4

		
N-N @ 6.2A	N-N @ 7.5 A	N-N @ 6.4A

Comparison of a 2D lead iodide crystalline structure with 2,4,4-trimethyl-1,6-hexanediamine

Crystalline structure of $[\text{NH}_3(\text{CH}_2)_6\text{NH}_3]\text{PbI}_4$ from [1] superimposed with rectangles sized to the true computed size of the organic molecule $\text{R}=2,4,4\text{-trimethyl-1,6-hexanediamine}$ (left isolated structure). Side and top view are placed below. It is evident that the organic molecule cannot be simply be inserted in the place of 1,6-hexanediamine, which would form the inorganic network of ref. [1]. Red and green rectangles superimposed on the [1] crystalline structure refer to the same organic molecule. Forming an inorganic network such as the red-gray below would require its significant deformation for the insertion of R.



Low temperature PL spectra

Compound **m1_ns2** at 77K (Fig. S18) has a different PL peak, from that of RT, located at 509 nm, and displays a broad peak at ca. 600 nm, while the PLE spectra reveal an absorption excitonic peak at ca. 500 nm. Thus, compared to RT spectra, the OA 2D excitonic peak has red shift while the 2D excitonic PL peak has blue shift.

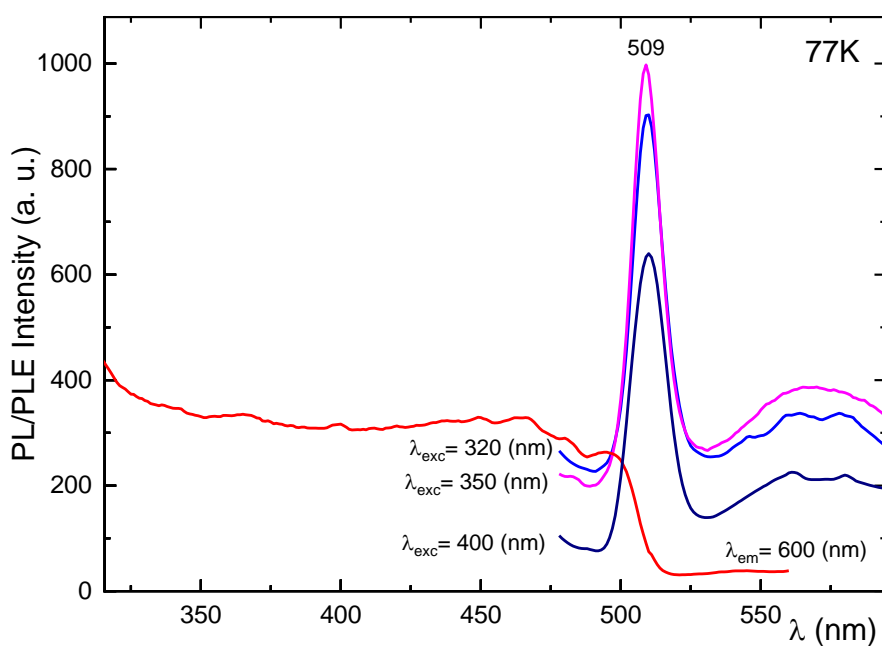


Figure S18. PL and PLE spectra for **m1_ns2** at $T = 77$ K.

Compound **m2** at 77K (Fig. S19) has a less broad PL peak, from that of RT, located at 407 nm, while the PLE spectra reveal an absorption excitonic peak at ca. 413 nm.

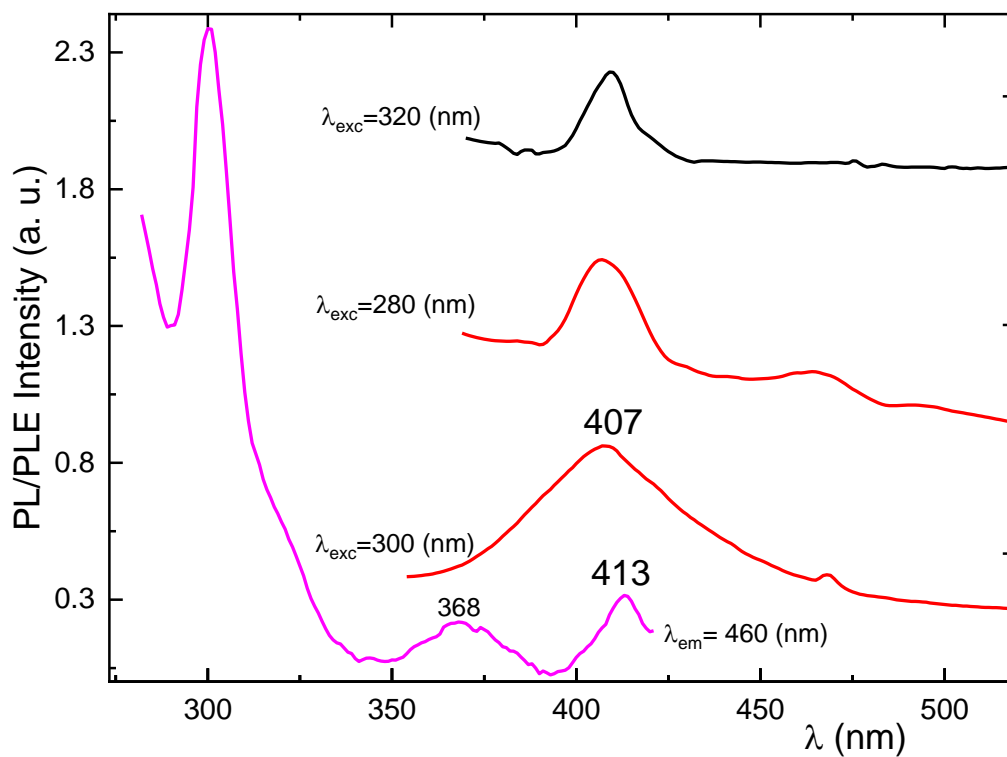


Figure S19. PL and PLE spectra for **m2** at 77 K.

Compound **m3**, as prepared, at low temperatures 77K shows (Fig. S20) only a broad PL signal centered at 500-546 nm, with its peak position being wavelength dependent. The PLE spectra, comparable to the OA spectra at RT, shows peaks at 300, 333 and 368 nm.

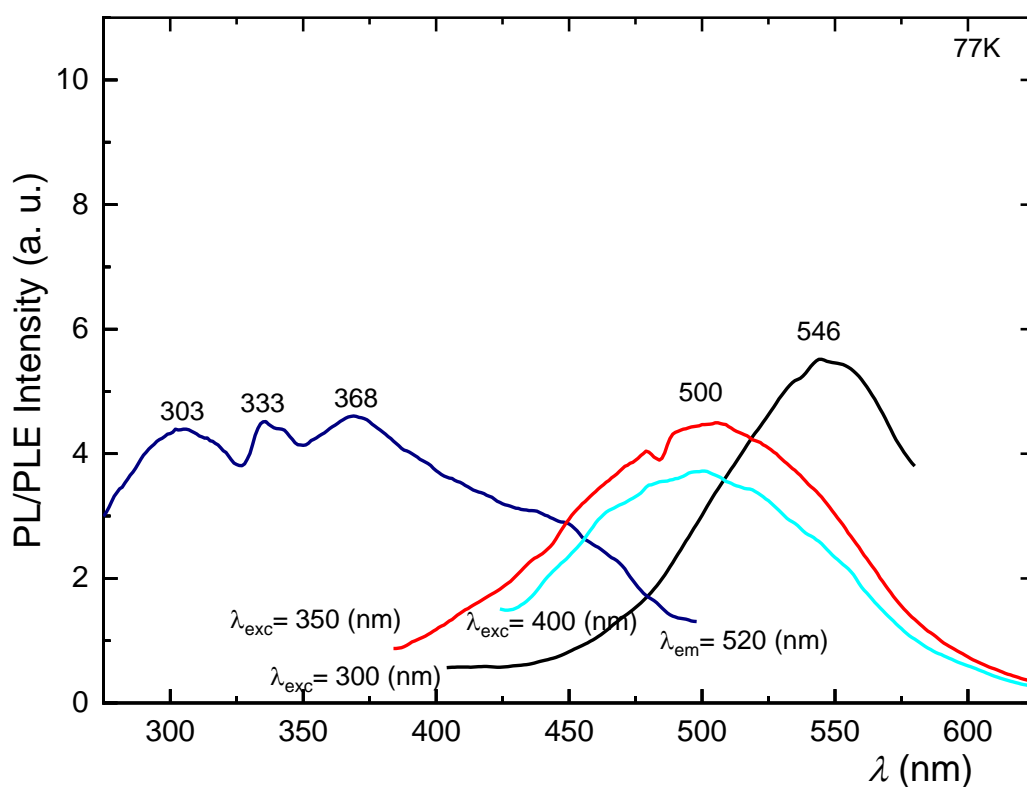


Figure S20. PL and PLE spectra for **m3** at 77 K.

¹ Mousdis G. A., Papavassiliou G. C., Raptopoulou C. P., Terzis A. *J. Mater. Chem.* 2000, 10, 515-518.