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Liquid reagents are not enough for liquid assisted grinding in the synthesis of $[(AgBr)(n\text{-pica})]_n$

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Supporting information

S1. Crystallographic data

Table S1. Crystallographic information of $[(AgBr)_2(n\text{-pica})]_n$.

	$[(AgBr)_2(3pica)]_n$	**$[(AgBr)_2(4pica)]_n$**
Empirical formula	$C_6H_8Ag_2Br_2N_2$	$C_6H_8Ag_2Br_2N_2$
Formula weight (g mol^{-1})	483.68	483.68
T (K)	293	293
Wavelength (Å)	0.71073	1.535
Crystal system	Monoclinic	Orthorhombic
Space group	C2/c	Pbca
a (Å)	24.605(3)	14.282(1)
b (Å)	6.2851(5)	22.011(1)
c (Å)	14.3050(12)	6.624(1)
β (°)	110.938(9)	90
V (Å^3)	2066.2(3)	2082
Z, Z’	8, 1	8,1
ρ_{calc} (mg m^{-3})	3.110	3.088
μ (mm^{-1})	11.474	
F(000)	1776	
crystal size (mm)	0.167×0.143×0.076	powder
ϑ range for data collection (◦)	3.360° to 28.984°	6° to 75°
reflections collected	4378	
Independent reflections	2359	
R_{int}/R-Bragg	0.0698	0.0337
Completeness to theta = 25.000°	99.8%	
Refinement method	Full-matrix least-squares on F^2	Rietveld
T_{max}/T_{min}	1.00000/0.16766	
data/restraints/parameters	2359 / 0 / 110	
Goodness-of-fit	0.991	1.08
R1 [I > 2σ(I)]/Rp	0.0726	0.0448
*w*R2 (all data)/Rwp	0.1277	0.0607

Table S2. Crystallographic information of $[(AgBr)(n\text{-pica})]_n$, already published here.[1]

	$[(AgBr)(3\text{-pica})]_n$	**$[(AgBr)(4\text{-pica})]_n$**
Empirical formula	$C_6H_8AgBrN_2$	$C_6H_8AgBrN_2$
Formula weight (g mol^{-1})	295.915	295.915
T (K)	293	293
Wavelength (Å)	0.71073	1.535
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	9.4518(6)	6.316
b (Å)	6.1880(3)	7.365
c (Å)	14.3981(9)	17.769
a (Å)	90	90
b (Å)	105.712(6)	81.08
g (Å)	90	90
V (Å^3)	810.64(8)	816
Z, Z’	4, 1	4, 1
ρ_{calc} (mg m^{-3})	2.425	2.407

S2. Rietveld refinement

A polycrystalline sample of $[(AgBr)_2(4\text{-pica})]_n$ was loaded into a 0.5 mm borosilicate glass capillary and transmission powder X-ray diffraction (PXRD) data were collected over the range 5°–75° 2θ (2 kW; Cu Kα1, 1.54056 Å; step size 0.017° 2θ), for a total of 6 hours. The Panalytical X’Pert PRO diffractometer was equipped with a Pixel detector. The data indexed to an orthorhombic cell were Pawley fitted in TOPAS6[2] and then the most probable space group of Pbca determined by use of the same program. A Chebyshev function and a pseudo-Voigt (TCHZ type) were used to fit the background and the peak shape, respectively Consideration of the cell volume, molecular volume, and space group symmetry suggested Z’ = 1. The validity of the structure was confirmed by a Rietveld refinement against data in the range 6°–70° 2θ using TOPAS6. The final Rietveld refinement yield an Rwp value of 6.1.

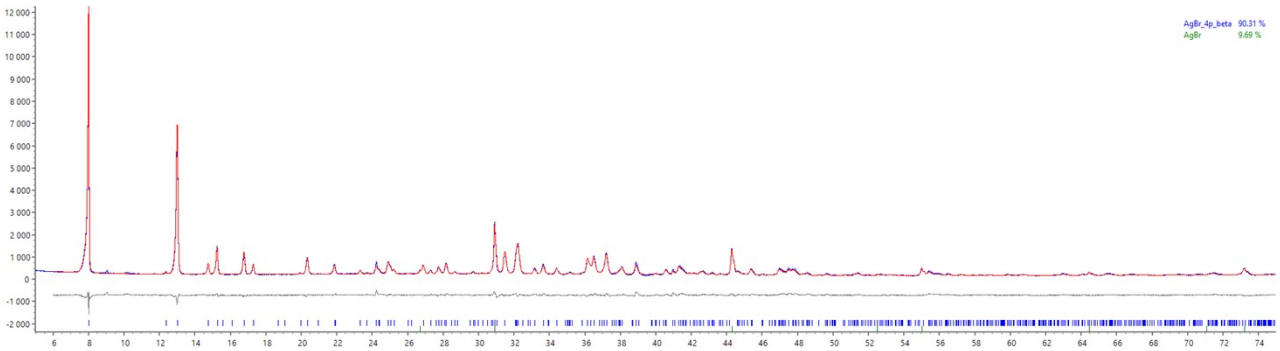

Figure S1. Rietveld refinement (red line) of $[(AgBr)_2(4\text{-pica})]_n$ diffraction pattern (blue line). Peaks of unreacted AgBr are present. In grey, the difference plot.

S3. DSC analysis

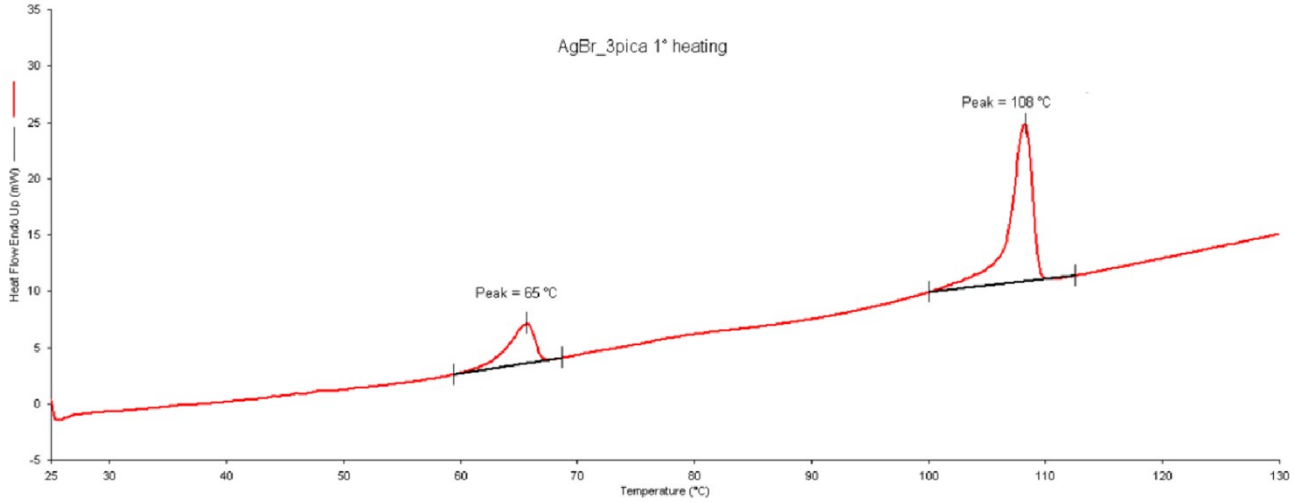

Figure S2. DSC curve of $[(AgBr)(3\text{-pica})]_n$. The endothermic peak observed at 65°C was identified as resulting from the partial loss of 3-pica and its conversion into $[(AgBr)_2(3\text{-pica})]_n$, while the peak at 108°C was attributed to the melting of the compound.

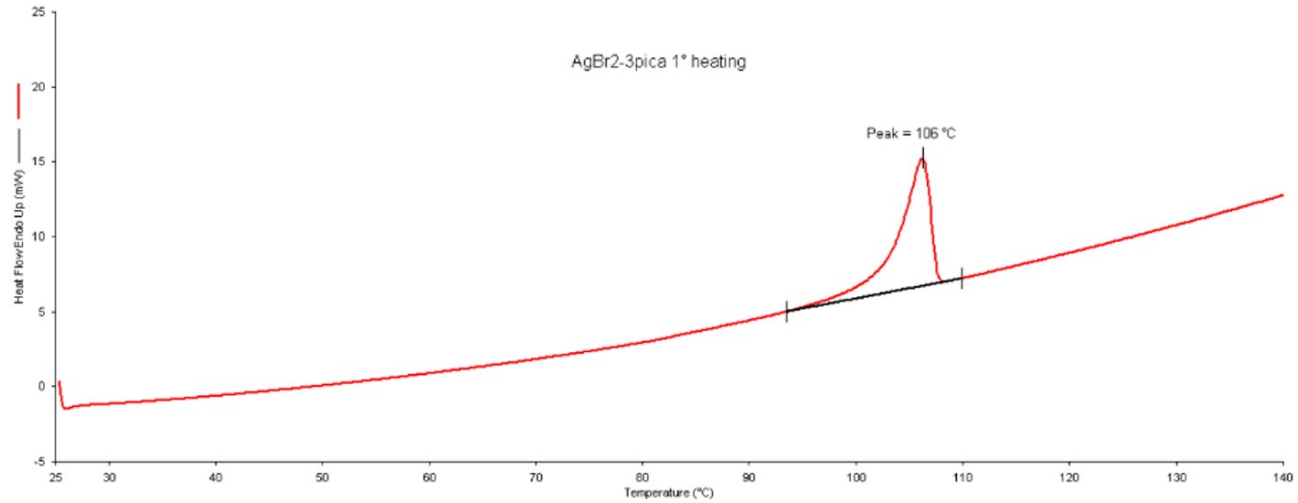

Figure S3. DSC curve of $[(AgBr)_2(3\text{-pica})]_n$ with melting at 106°C.

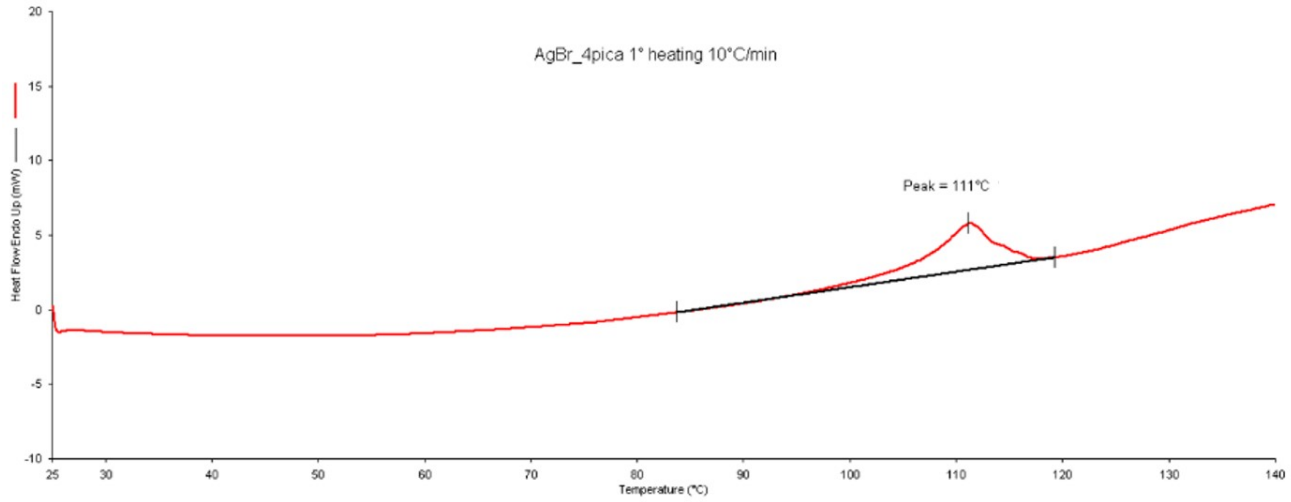

Figure S4. DSC curve of $[(AgBr)(4\text{-pica})]_n$. It exhibits only an endothermic peak at 111°C which is attributed to the melting of the compound and hence the thermal conversion of the 1:1 phase into the 2:1 is not observed.

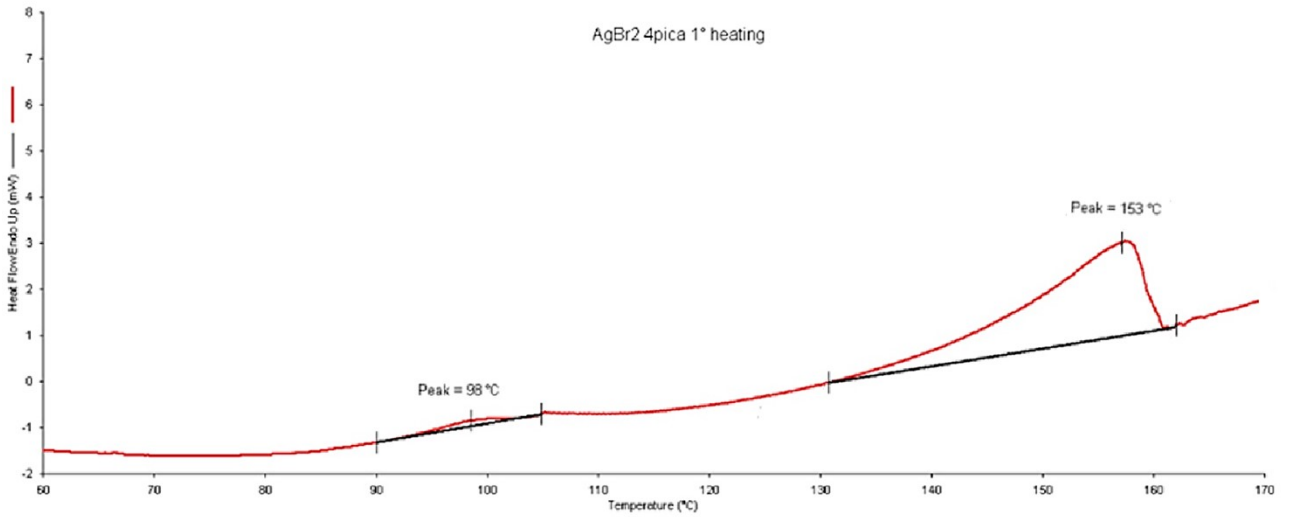

Figure S5. DSC curve of $[(AgBr)_2(4\text{-pica})]_n$, the endothermic peak at 98°C was attributed to partial loss of 4-pica before the melting at 153°C.

S4. TGA analysis

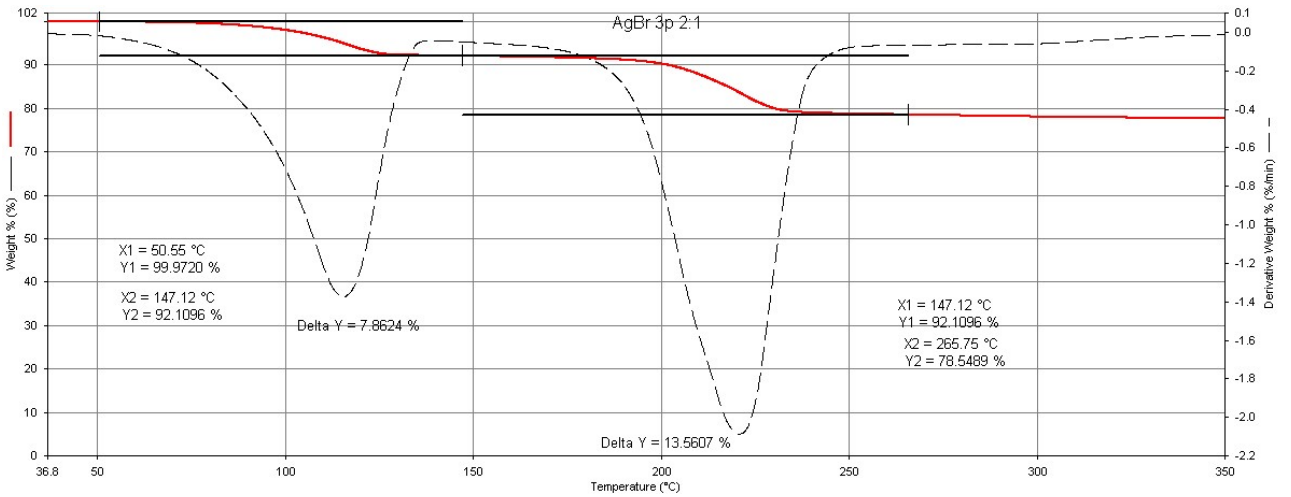

Figure S6. TGA analysis of $[(AgBr)_2(3\text{-pica})]_n$

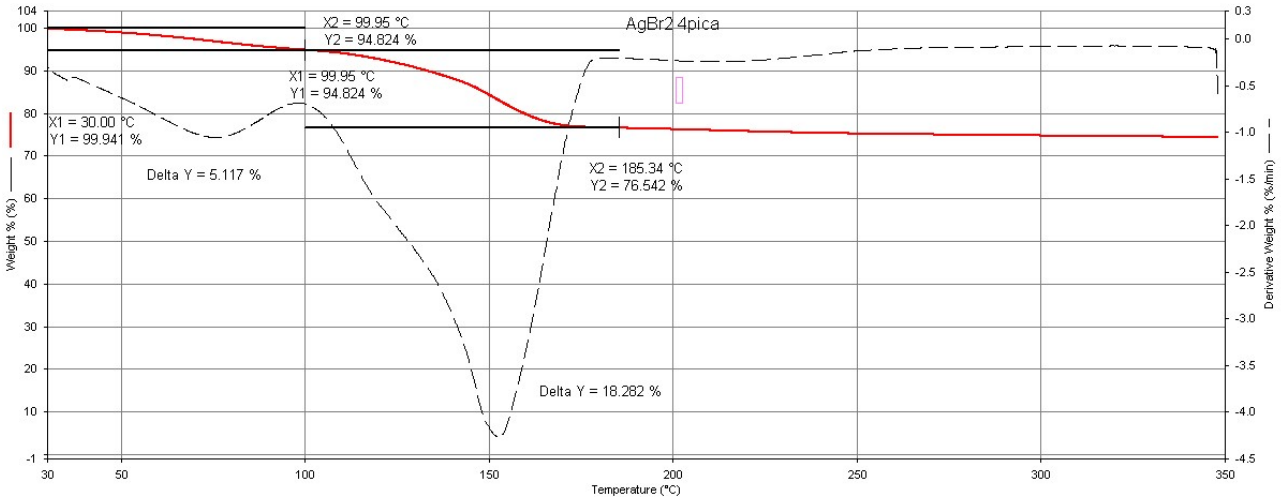

Figure S7. TGA analysis of $[(AgBr)_2(4\text{-pica})]_n$.

S5. Mechanochemical synthesis and conversion of the phases

The powders obtained by grinding for 60 minutes 1.0 mmol of AgBr with different amounts of 3-pica were analyzed and the different phase quantified by Rietveld refinement. 1:1 and 2:1 phases correspond to $[(AgBr)(3\text{-pica})]_n$ and $[(AgBr)_2(3\text{-pica})]_n$ respectively. The synthesis with 0.07 and 0.08 mL of 3-pica were repeated 3 times, and the average values were reported in the graph.

Table S3. Summary table of **Fig 6.** The mass percentages of the composition were determined by conducting Rietveld refinement on the powder diffraction data obtained using the X'Pert HighscorePlus program.[3] The reactions in stoichiometric ratio are highlighted in bold.

AgBr (mmol)	3-pica (mL)	3-pica (mmol)	1:1 %	2:1 %	Unreacted AgBr %
1.0	0.01	0.1	0	20	80
1.0	0.02	0.2	0	42	58
1.0	0.03	0.3	0	61	39
1.0	0.04	0.4	0	93	8
1.0	**0.05**	**0.5**	**0**	**94**	**6**
1.0	0.06	0.6	0	97	3
1.0	0.07	0.7	37	60	4
1.0	0.08	0.8	63	36	2
1.0	0.09	0.9	73	24	4
1.0	**0.10**	**1.0**	**94**	**5**	**2**
1.0	0.15	1.5	99	0	1
1.0	0.20	2.0	99	0	1
1.0	0.30	3.0	100	0	0

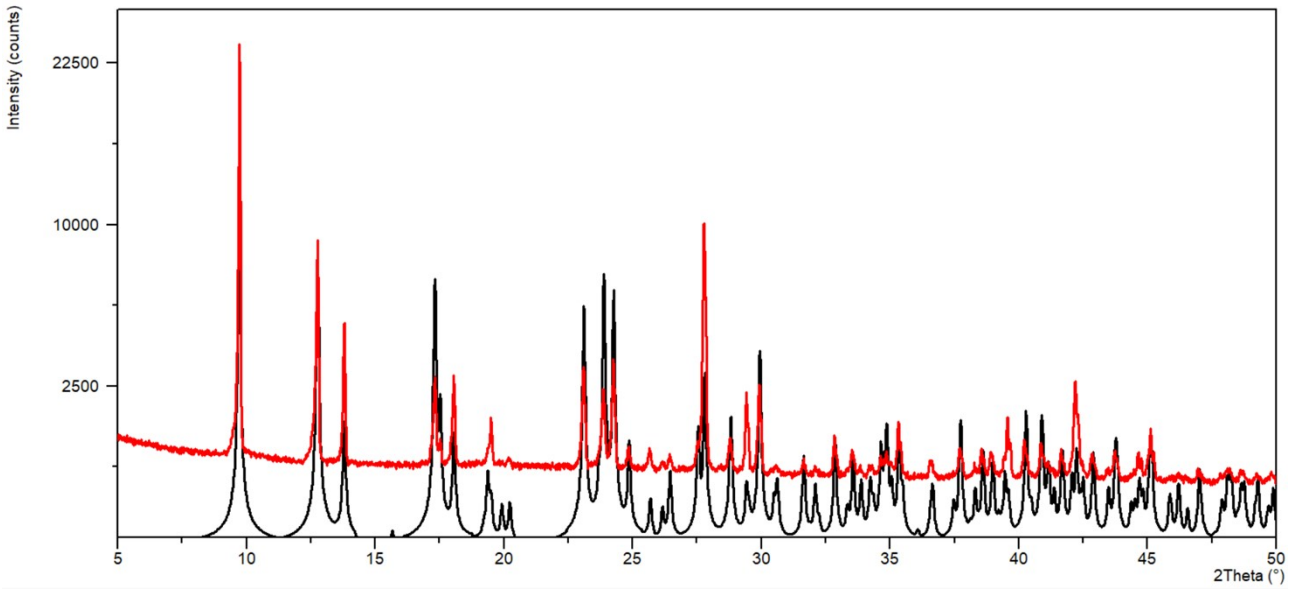

Figure S8. Comparison between calculated (black line) and experimental (red line) X-ray powder diffraction patterns of $[(AgBr)(3\text{-pica})]_n$, obtained by grinding 1 mmol of AgBr, 2 mmol of 3-pica and 0.02 mL of acetonitrile. No unreacted AgBr is present in the powder.

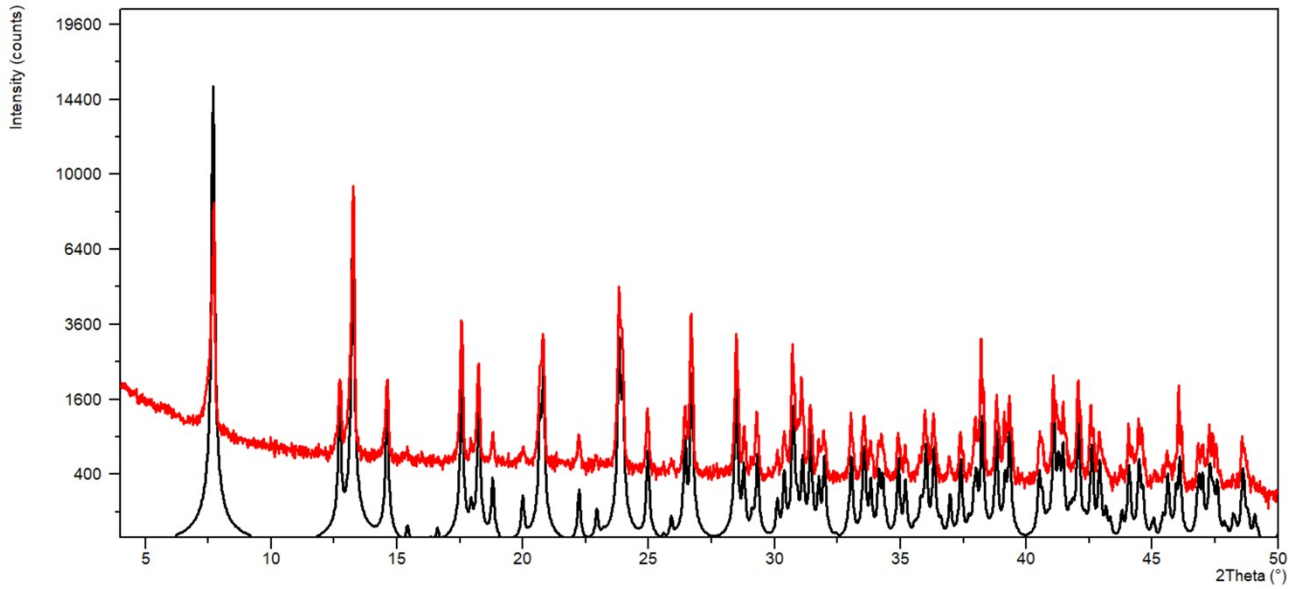

Figure S9. Comparison between calculated (black line) and experimental (red line) X-ray powder diffraction patterns of $[(AgBr)_2(3\text{-pica})]_n$, obtained by grinding 1 mmol of AgBr, 0.6 mmol of 3-pica and 0.02 mL of acetonitrile. No unreacted AgBr is present in the powder.

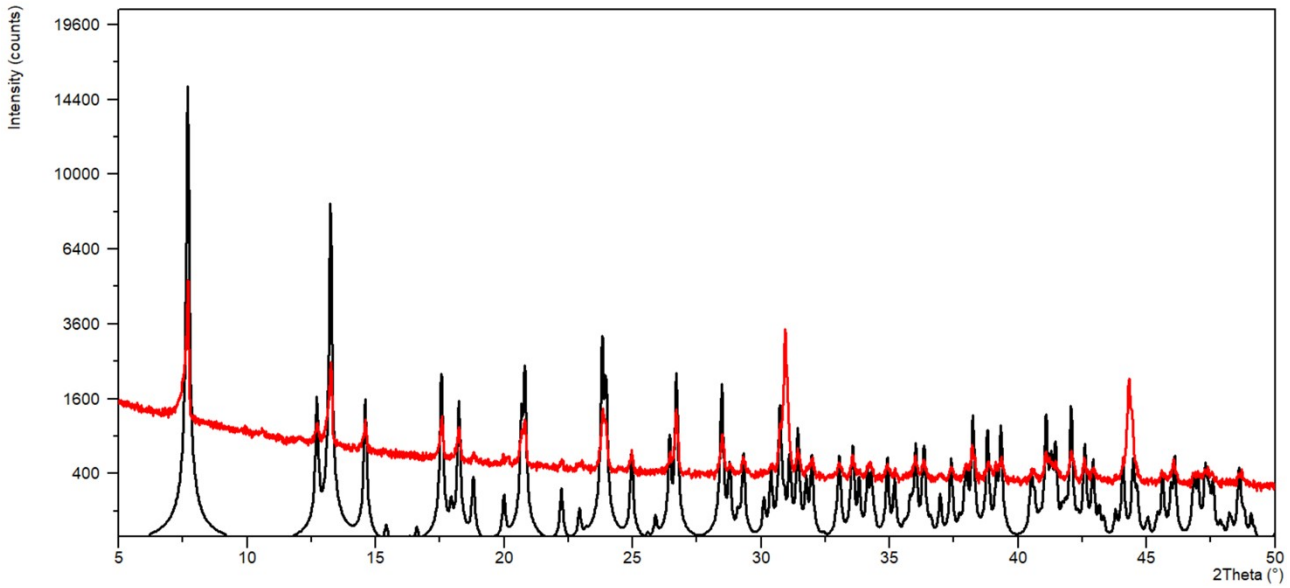

Figure S10. Comparison between experimental (red line) and calculated (black) pattern of $[(AgBr)_2(3\text{-pica})]_n$ X-ray powder diffraction patterns. The powder was obtained by grinding $[(AgBr)(3\text{-pica})]_n$, with AgBr. The peaks at $2\theta = 30.97°$ and 44.33° belong to AgBr.

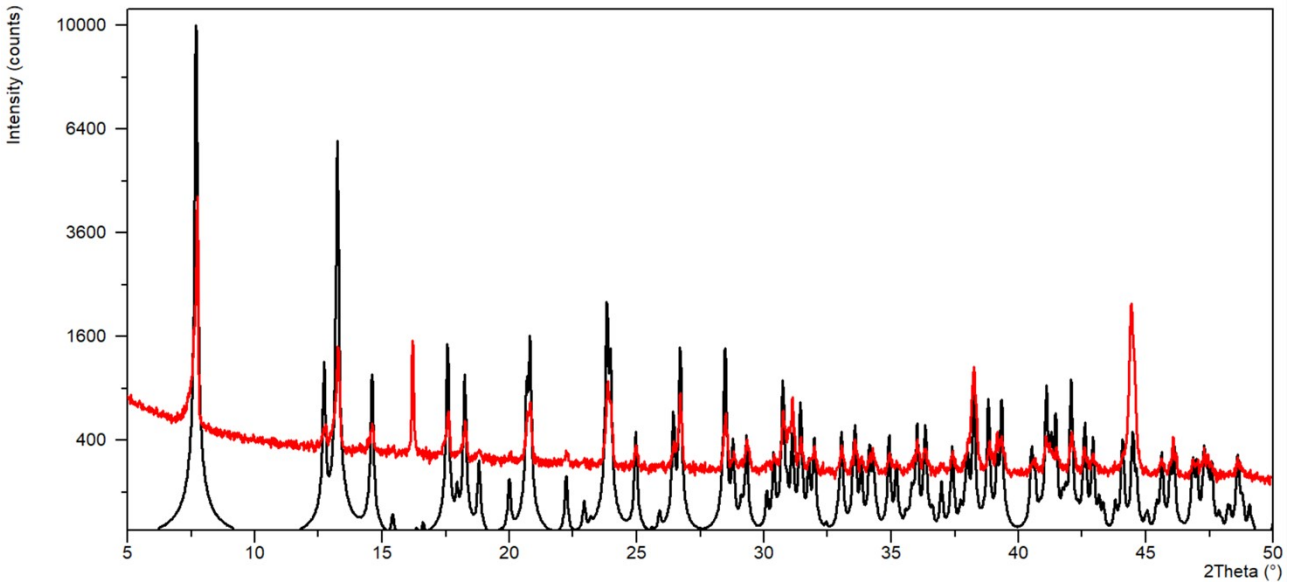

Figure S11. Comparison between experimental (red line) and calculated (black) pattern of $[(AgBr)_2(3\text{-pica})]_n$ X-ray powder diffraction patterns. The powder was obtained by heating $[(AgBr)(3\text{-pica})]_n$, at 65°C for one hour. The peaks at $2\theta = 30.97°$ and 44.33° belong to AgBr, the peak at $2\theta = 16.25°$ belongs to the sample holder.

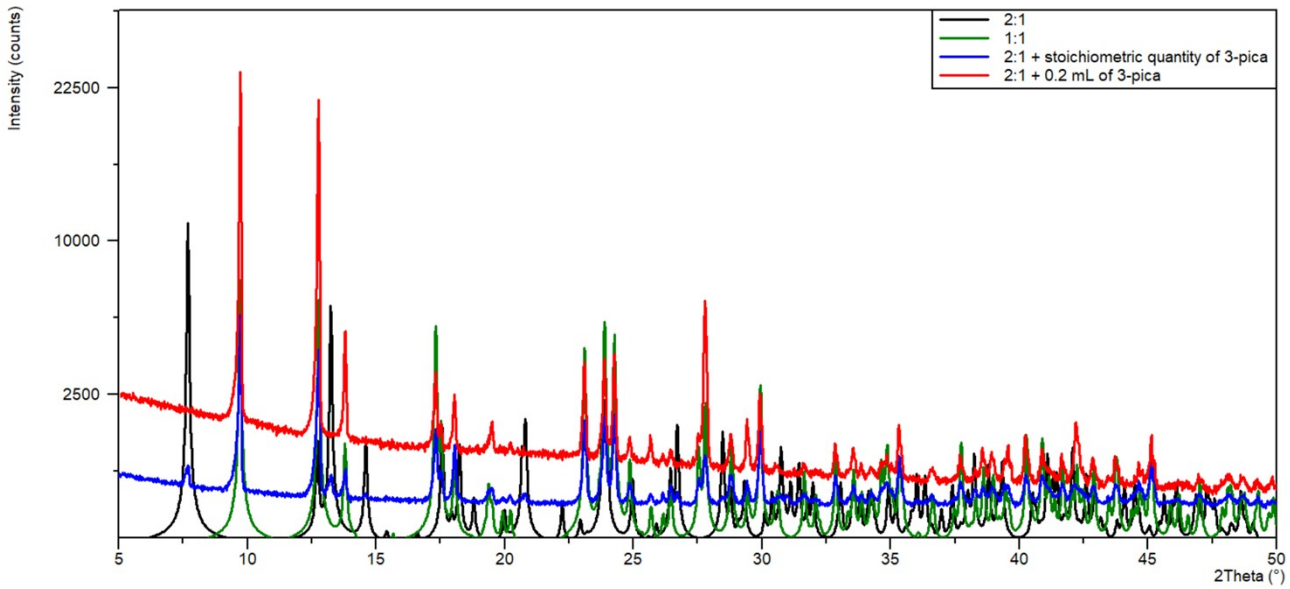

Figure S12. Comparison between X-ray powder diffraction patterns of $[(AgBr)_2(3\text{-pica})]_n$, after the grinding reaction with a stoichiometric quantity of 3-pica (blue line) to obtain $[(AgBr)(3\text{-pica})]_n$, the pattern correspond to a mixture of the two phases by adding a large excess of 3-pica the full conversion was obtained (red line). The calculated pattern of the $[(AgBr)(3\text{-pica})]_n$ phase is in green, the one of $[(AgBr)_2(3\text{-pica})]_n$ is in black.

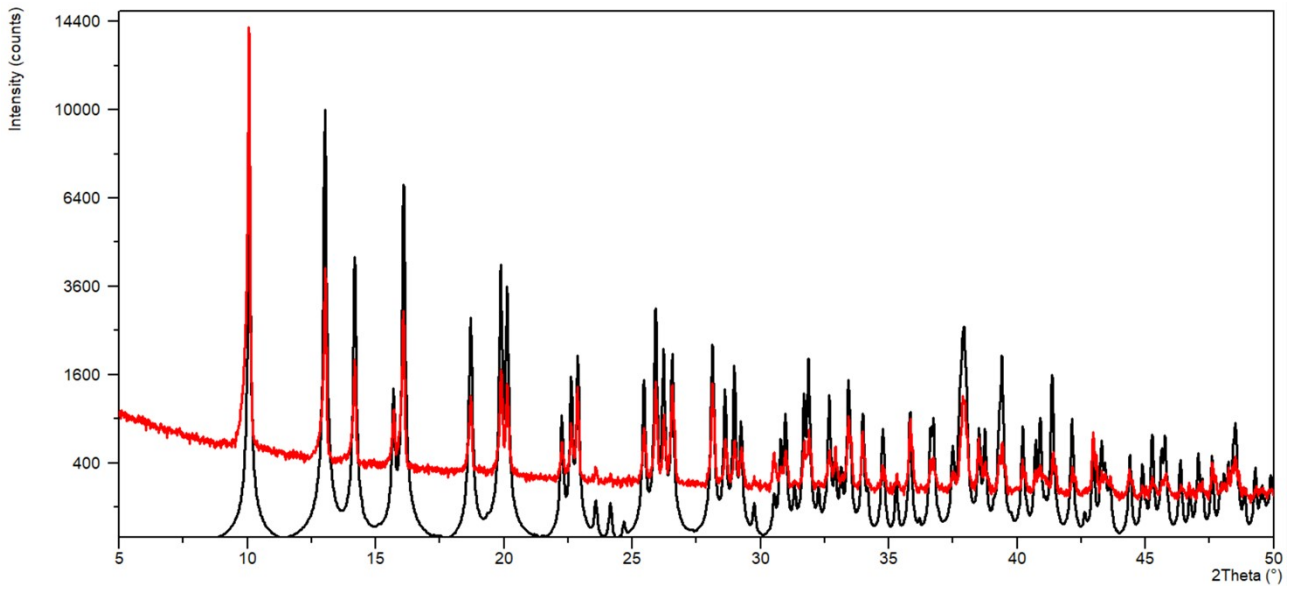

Figure S13. Comparison between calculated (black line) and experimental (red line) X-ray powder diffraction patterns of $[(AgBr)(4\text{-pica})]_n$, the 1:1 phase, obtained by grinding 1 mmol of AgBr and 2 mmol of 4-pica. No unreacted AgBr is present in the powder.

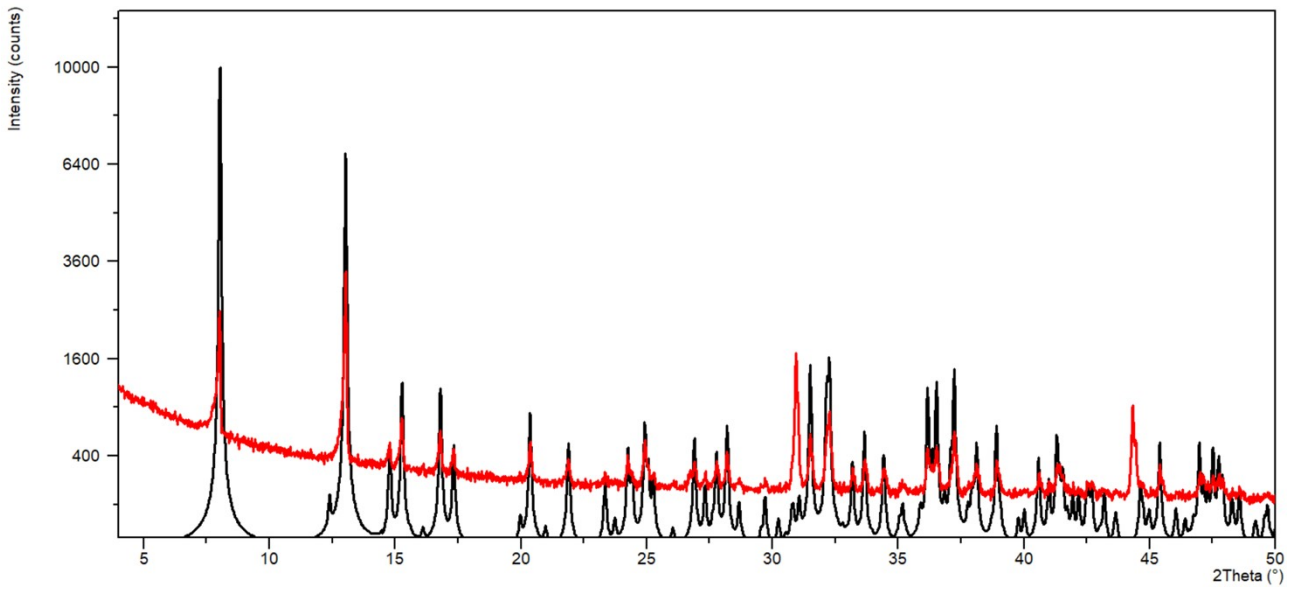

Figure S14. Comparison between calculated (black line) and experimental (red line) X-ray powder diffraction patterns of $[(AgBr)_2(4\text{-pica})]_n$, the 2:1 phase. The peaks at 2θ = 30.97° and 44.33° belong to AgBr.

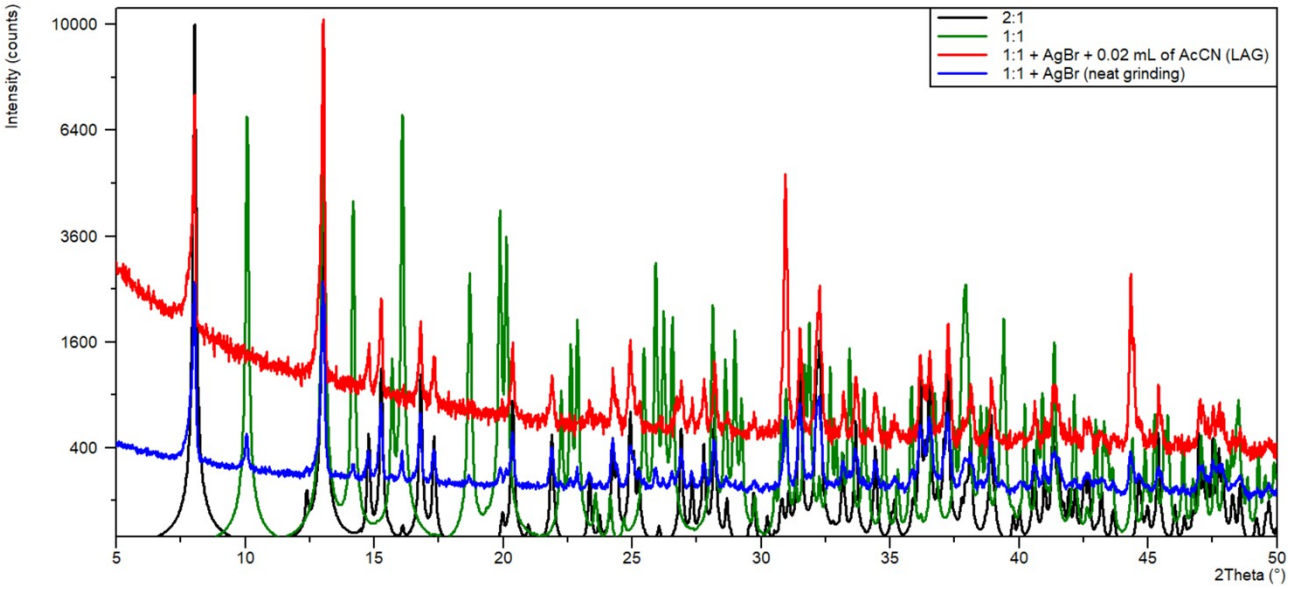

Figure S15. Comparison between X-ray powder diffraction patterns of $[(AgBr)_2(4\text{-pica})]_n$, the 2:1 phase; after the neat grinding reaction with a stoichiometric quantity of AgBr (blu line) and after the LAG reaction with acetonitrile (AcCN) (red line). The peaks at 2θ = 30.97° and 44.33° belong to AgBr. The calculated pattern of the 1:1 phase is in green, the one of the 2:1 phase is in black.

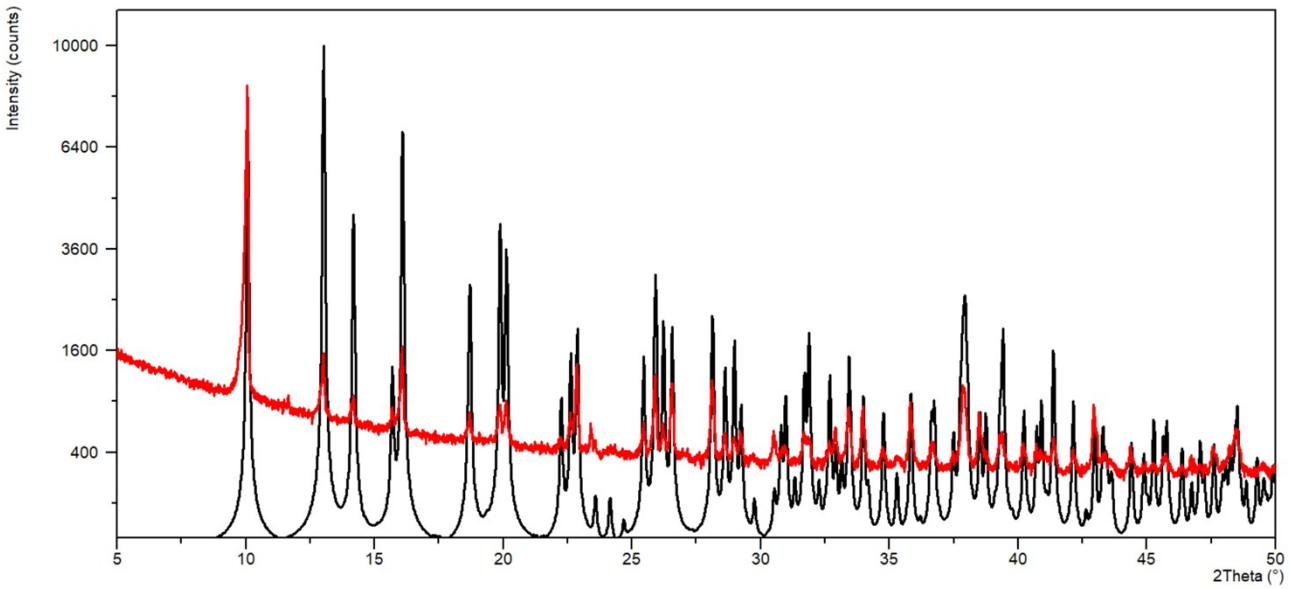

Figure S16. Comparison between experimental (red line) X-ray powder diffraction patterns of $[(AgBr)_2(4\text{-pica})]_n$, the 2:1 phase, after the grinding reaction with 4-pica, and calculated (black) pattern of $[(AgBr)(4\text{-pica})]_n$, the 1:1 phase.

References

1 C. Zuffa, C. Cappuccino, M. Marchini, L. Contini, F. Farinella and L. Maini, *Faraday Discuss.*, 2023, **241**, 448–465.

2 A. A. Coelho, *J. Appl. Crystallogr.*, 2018, **51**, 210–218.

3 T. Degen, M. Sadki, E. Bron, U. König and G. Nénert, *Powder Diffr.*, 2014, **29**, S13–S18.