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Supporting Information

The Key Role of the Interface in the Highly Sensitive Mechanochromic Luminescence Properties of Hybrid Perovskites

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Supporting File

Methods.

Synthesis.

All starting materials were of analytical grade and obtained from commercial sources without further purification (lead bromide ≥ 99%(Sigma-Aldrich); γ-Aminobutyric acid ≥ 99 (Sigma-Aldrich); and hydrobromic acid 48% in water (Sigma-Aldrich).

Synthesis of CH_3NH_3Br . CH_3NH_3Br was synthesized by reaction of the methylamine with the corresponding acid (HBr) : First, methylamine in absolute ethanol was stirred and cooled to 0°C with the addition of acid. The reaction solution was stirred for 2 h.Then rotary evaporation was applied to evaporate the solvent with a pressure of 0.1 MPa at 45°C. The precipitate was washed three times with diethyl ether and dried under vacuum (60°C, 5 h) for future use.

Samples prepared by precipitation. Two different stoichiometries were tried. A first with 2 equivalents **(50 mg)** of $HO_2C(CH_2)_3NH_2$, 1 equivalent **(27.1 mg)** of CH_3NH_3Br and 2 equivalents **(177.9 mg)** of $PbBr_2$ (stoichiometry 2-1-2) and a second with a 2-2-3 ratio **(50 mg / 54.9 mg / 266.9 mg)**. The first formally corresponds to the crude formula of the bilayer perovskite $((HO_2C(CH_2)_3NH_3)_2(CH_3NH_3)Pb_2Br_7$ and the second to the formula of the three-layer perovskite $((HO_2C\ (CH_2)_3NH_3)_2(CH_3NH_3)_2Pb_3Br_{10}$.

The reagents were dissolved in concentrated HBr **(10 to 20 drops)** and the anti-solvent which causes the precipitation is ethyl acetate. Powders were obtained, filtered off, washed several times with ethyl acetate and heated at 45°C for 20 minutes.

In both cases, an orange solid is recovered and analyzed by X-ray diffraction and solid state NMR. It appeared that mixtures of phases, or composite, consisting of $(HO_2C(CH_2)_3NH_3)_2PbBr_4$ ($(GABA)_2PbBr_4$) and $CH_3NH_3PbBr_3$ (3D) were obtained.

Chemical analysis (C, O, N, H) were carried out on the 2D-C4/3D composite obtained from $HO_2C(CH_2)_3NH_2$, CH_3NH_3Br and $PbBr_2$ in 2-1-2 stoichiometry. The results show that the obtained stoichiometry in the solid state, that is one $(HO_2C(CH_2)_3NH_3)_2PbBr_4$ for one $CH_3NH_3PbBr_3$, well corresponds to the stoichiometry in solution. (experimental values : mass% in C, O, N and H of 6.79, 2.28, 3.26 and 1.69, respectively *vs* theoretical values (1 $(HO_2C(CH_2)_3NH_3)_2PbBr_4$ / 1 $CH_3NH_3PbBr_3$) of 6.47, 2.33, 3.22, and 1.66, respectively).

Solid state NMR and X-ray powder diffraction.

X-Ray powder diffraction (XRPD) analyses were performed at room temperature using a D8 Bruker diffractometer (Cu Ka,l= 1.5418 Å) equipped with a linear Vantec super speed detector. It has been shown that all the observed reflections could be indexed to the unit cell parameters obtained from single crystal X-ray diffraction experiments for the two phases **$(GABA)_2PbBr_4$** and **$CH_3NH_3PbBr_3$**. Solid state NMR spectra have been acquired on a Bruker Avance III WB 300 MHz (7.4 T) spectrometer equipped with a 4 mm VTN probe. The samples were spun under the magic angle with 5 kHz. The ^{13}C spectra shown in the article have been acquired as direct excitation experiment with a DEPTH sequence to suppress background signals. 1 K scans have been acquired with a recycle delay of 40 s. A 10 Hz exponential window function has been applied before Fourier transform.

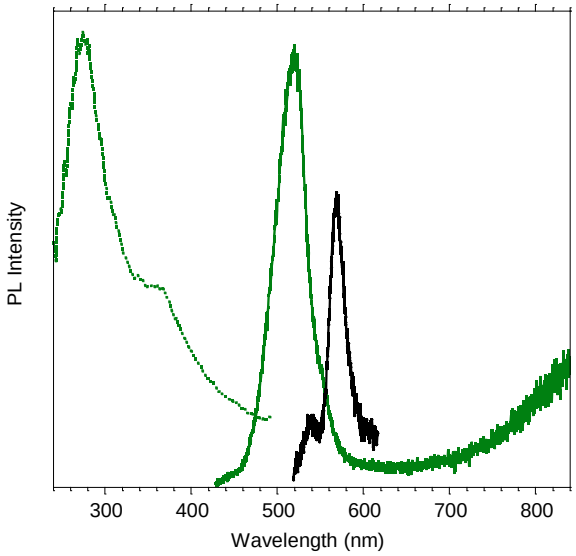
Spectroscopy. UV-Vis spectra are obtained with a Perkin-Elmer Lambda900 spectrometer. Photoluminescence spectra are obtained with a NanoLog composed by a iH320 spectrograph equipped with a Synapse QExtra charge-coupled device by exciting with a monochromated 450 W Xe lamp. Phosphorescence (Ph) spectra are obtained with PPD-850 single photon detector module with Time-Gated Separation by exciting with a pulsed Xe lamp. The spectra are corrected for the instrument response. PL QY were measured with a home-made integrating sphere according to the procedure reported elsewhere [J. Moreau at al. Chem.Phys.Chem. 10, 647-653 (2009)]. Time-resolved TCSPC measurements are obtained with a PPD-850 single photon detector module and DeltaTime serie DD-300 DeltaDiode and DD-405L DeltaDiode Laser and analysed with the instrument software DAS6.

Table S1 Emission properties of the compounds

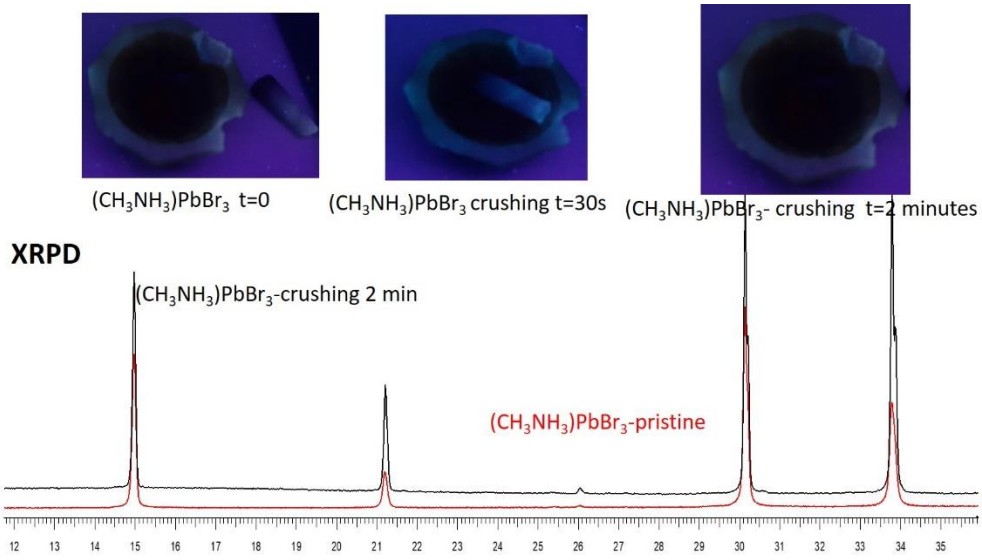
Photoluminescence (PL), PL excitation (PLE) and Phosphoresence (Ph) maximum positions, PL quantum Yeld (QY)

	PLE/nm	PL/nm	QY % λ_{exc}=360nm	PL lifetime/ns λ_{exc}=300nnm	CIE	Ph	Ph lifetime/ms (λ_{exc})
2D-C4	280,373 280,395	390 412	15.6	7.1 10.2	0.22;0.21	410,390w 550	0.41,0.33 1.34 (290 nm)
2D-C4/3D[a]	277,369 277,360,394 277,360,394 277,360,395	393 405vw 440vw 578	8	11.2	0.38;0.35	397,500w 580	-- 2.25 (300nm)
2D-C4/3D[a] crushed	278,369 278,362,393 276,385 278,360,399,440	390 405w 441 526	7	5.7 -- 45.9 74.5	0.20;0.53	397,446 529 585	-- 0.42 (395nm) 1.87 (395nm)
2D-C4/3D[b]	279,360, 279,360,395	392 573				570	2.47 395nm)
2D-C4/3D[b] crushed	290,325,379 290,325,379,390 280,310,350,405,460,510 280,310,350,405,460,510	390 445 525 545				500 sh 560	1.33 (300nm) 2.82 (395nm)
3D	----	537, 568					
3D crushed	275, 360	536					

[a]from solution; [b]from solid state; [sh]shoulder; $\tau_{av}=\sum_i \frac{Aiti^2}{Aiti}$



-a-



-b-

Figure S1. PL of crystallized powders of $(CH_3NH_3)PbBr_3$. a) PL spectra of 3D $(CH_3NH_3)PbBr_3$ crystallized powder before (black line) and after (green line) strong grinding (t > 2min, λ_{exc}=350 nm). PLE spectrum (green dashed line, (λ_{em}= 520 nm) after strong grinding; b) Photos (upon UV lamp) of $(CH_3NH_3)PbBr_3$ along with crushing and X-ray powder diffraction patterns.

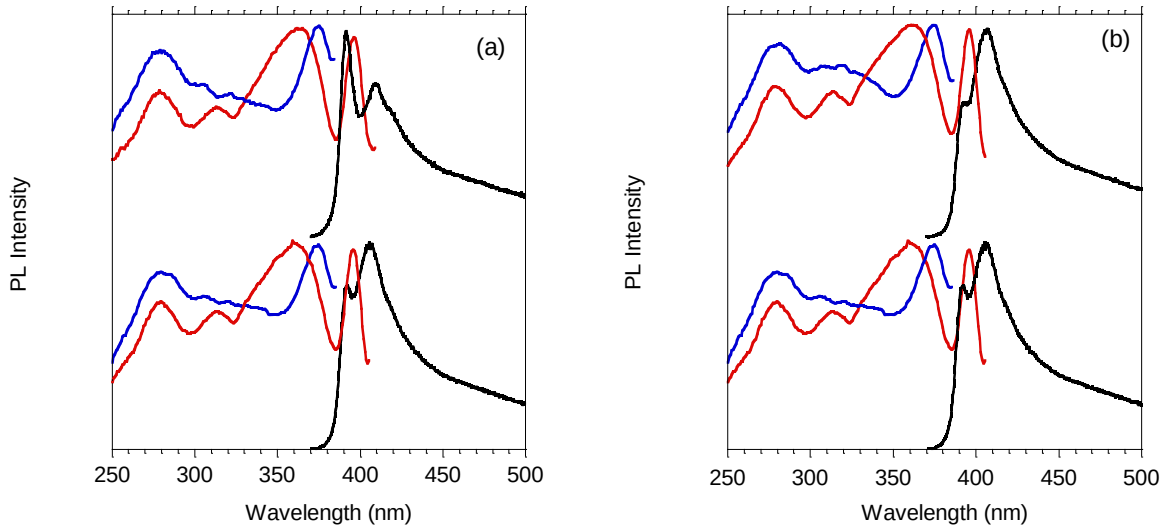
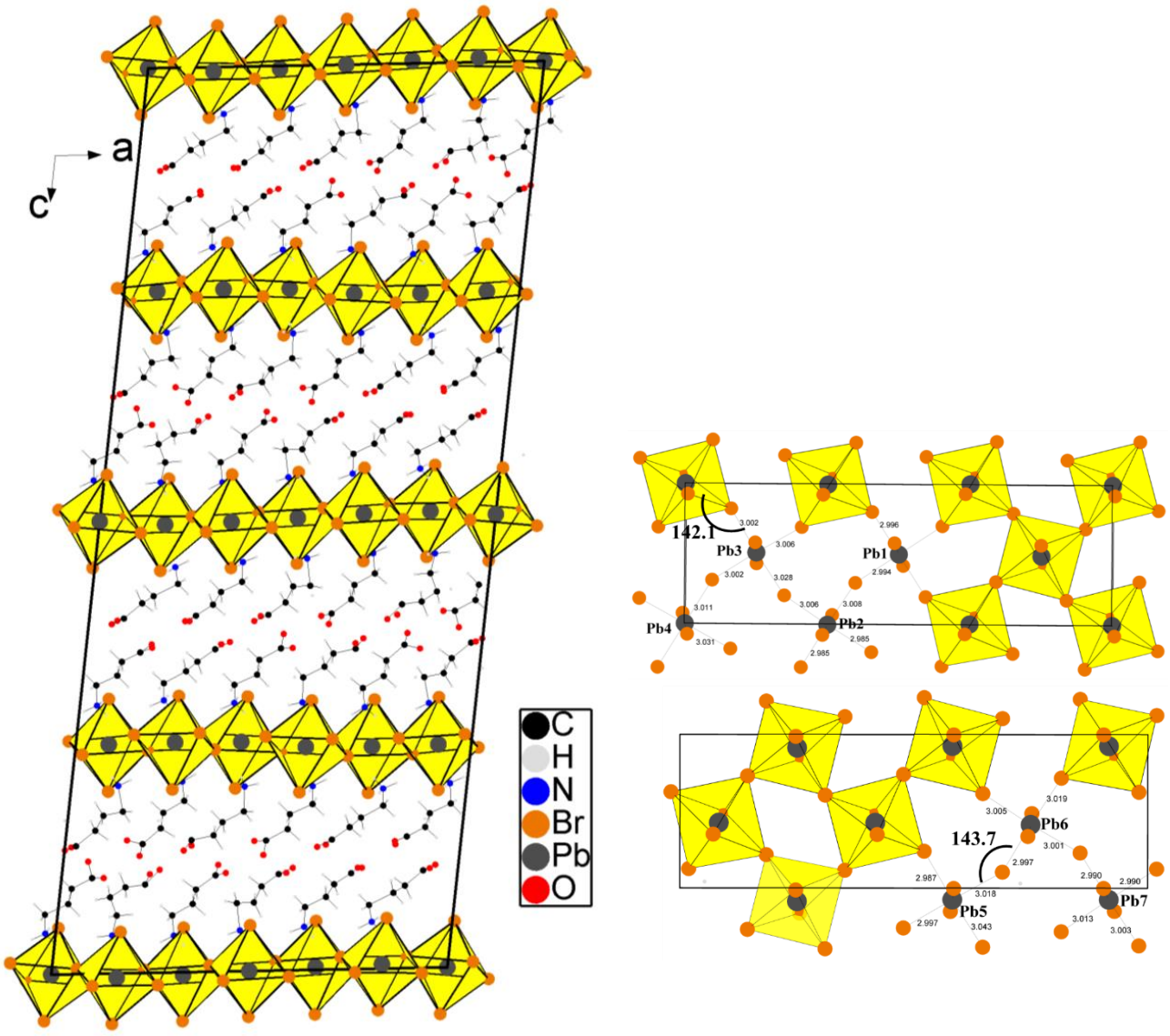
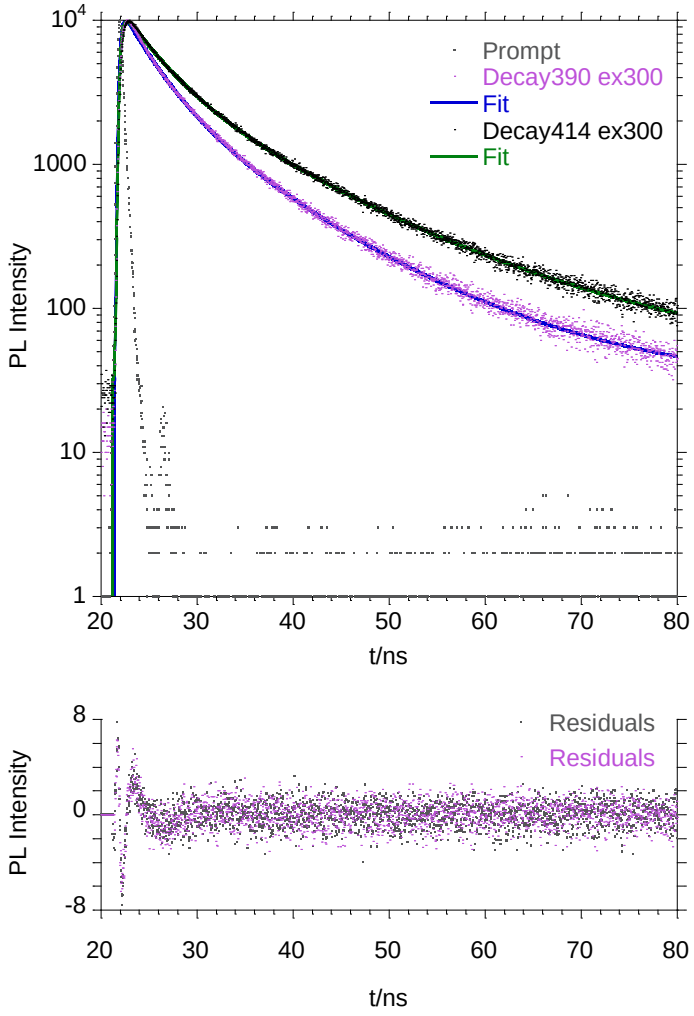


Figure S2 PL spectra (black line, excitation 310 nm) and PLE spectra (blue line, λ_{em}= 395 nm; red line λ_{em}= 407nm) of $(GABA)_2PbBr_4$ single crystals (a) before (top) and after (bottom) crushing (incidence angle 0°). (b) After crushing at incidence angle of 45° (top) and 0° (bottom).



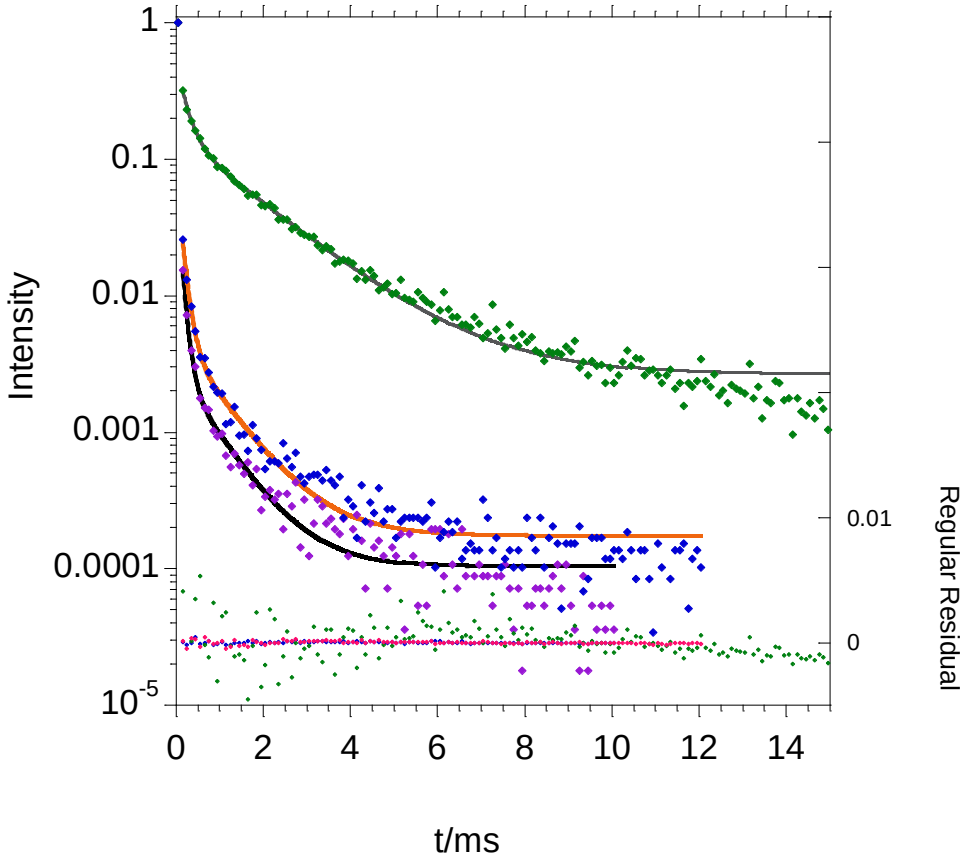
-a- **-b-**

Figure S3 Structure of $(GABA)_2PbPr_4$ (2D-C4): general view showing out-of-plane distortions of perovskite layers (a) and view of layers showing in-plane distortions (b) .



	B1	B2	B3	T1	T2	T3	<t> /ns	τ_{av} /ns	chisquare
em390	0,015	0,034606	0,005401429	6,720851	2,829256	13,36854	4,925	7,0863	1,501987
em414	0,016657	0,031866	0,002454069	10,07544	3,483794	23,54333	6,603	10,213	1,544223

Figure S4. PL decays of crystallized powder of $(GABA)_2PbBr_4$. λ_{ex}= 300 nm, three-exponential fit $\sum_{i=1,3} Bi.exp(\frac{t}{Ti})$. Average lifetimes <t>= $\sum_i \frac{Aiti}{Ai}$; $\tau_{av} = \sum_i \frac{Aiti^2}{Aiti}$



emission	y0	A1	t1	A2	t2	Adj. R-Square	<t> /ms	τ_{av} /ms
550nm	0,00266	0,36632	0,2085	0,14815	1,69022	0,99852	0,635185	1,343904
413nm	1,74E-04	0,00494	0,94125	0,06941	0,1267	0,99753	0,180821	0,408422
393nm	1,03E-04	0,05156	0,10842	0,00278	0,86014	0,99741	0,146878	0,333634

Figure S5. Phosphorescence decays of crystallized powder of $(GABA)_2PbBr_4$. λ_{ex}= 290 nm, λ_{em}= 393 nm (pink dots); λ_{em}= 413 nm (blue dots); λ_{em}= 550 nm (green dots); bi-exponential fits $\sum_{i=1,2} Ai.exp(\frac{t}{ti})$

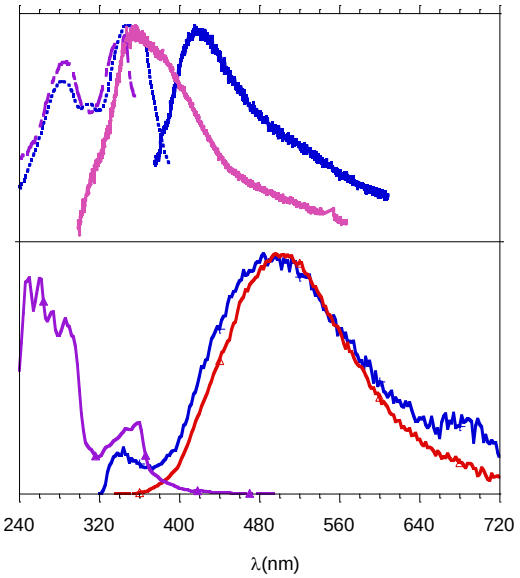
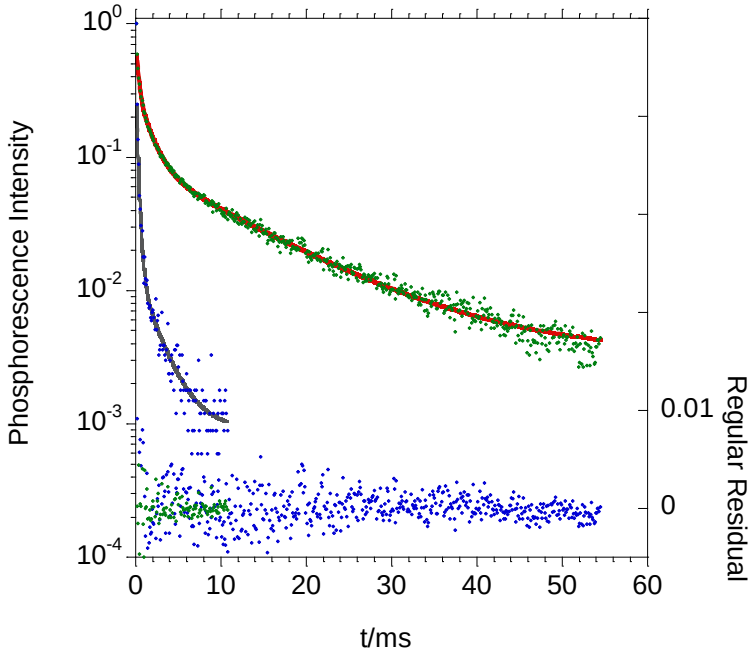
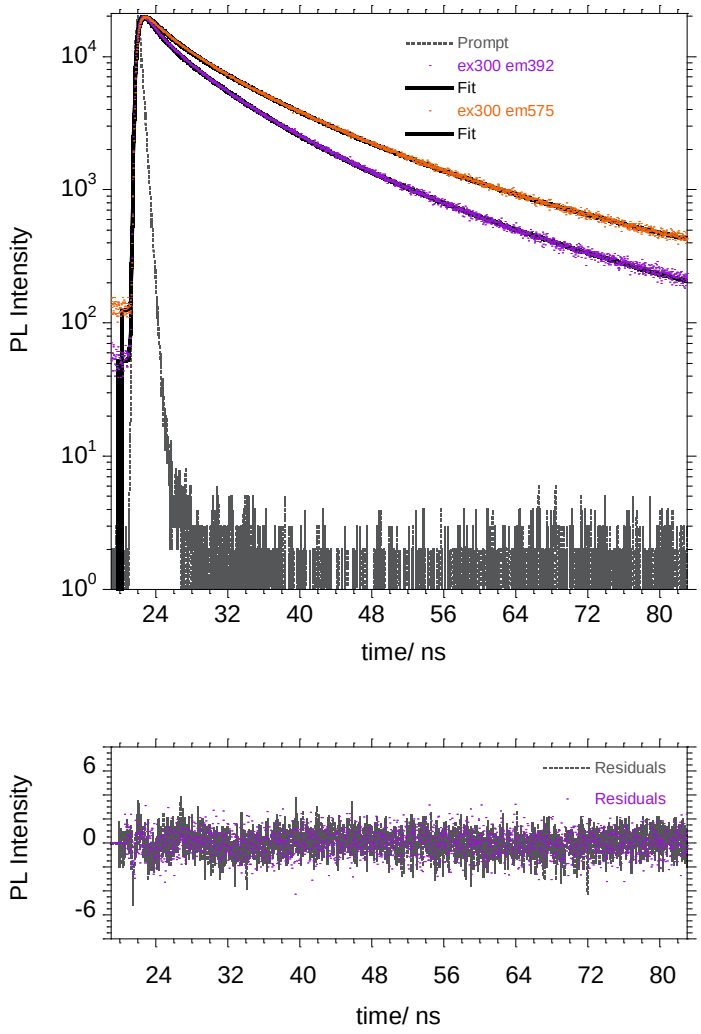


Figure S6. Photoluminescence (top) and phosphorescence (bottom) spectra of (GABA)Br ((C4)Br) acid salt Top: λ_{ex}= 275 nm, pink solid line; λ_{ex}= 345 nm, blue solid line; λ_{em}= 385 nm, pink dashed line; λ_{em}= 385 nm, blue dotted line. Bottom: λ_{ex}= 290 nm, delay 0.1, window 0.2 ms, blue solid line; delay 1 ms window 5 ms, pink line; λ_{em}= 510 nm, delay 1 ms window 5 ms.



	A1	t1	A2	t2	A3	t3	Adj. R-Square	<t> ms	τ_{av} ms
em350	0,5567	0,10557	0,1714	0,29092	0,0134	2,23941	0,99794	0,19	0,63
em510	0,08634	11,92559	0,24732	1,48409	0,50368	0,24171	0,99868	1,81	8,46

Figure S7 Phosphorescence decays of C4 (GABA)Br acid salt λ_{ex}= 290 nm, λ_{em}= 350 nm, blue dots; λ_{em}= 510 nm, green dots. Three-exponential fit $\sum_{i=1,3} Ai.exp(\frac{t}{ti})$



	B1	B2	B3	T1	T2	T3	<t> ns	τ_{av} ns	chisquare
em393	0,02131	0,015568	0,007523472	6,583428	1,465863	17,70507	6,67	11,19	1,81392
em575	0,020269	0,011583	0,00844453	8,622773	2,34988	21,1259	9,44	14,04	1,05896

Figure S8. PL decays of pristine 2D-C4/3D composite obtained by solution process. λ_{ex}= 300 nm, λ_{em}= 392 nm (pink), λ_{em}= 575 nm (orange).Three-exponential fit $\sum_{i=1,3} Bi.exp(\frac{t}{Ti})$

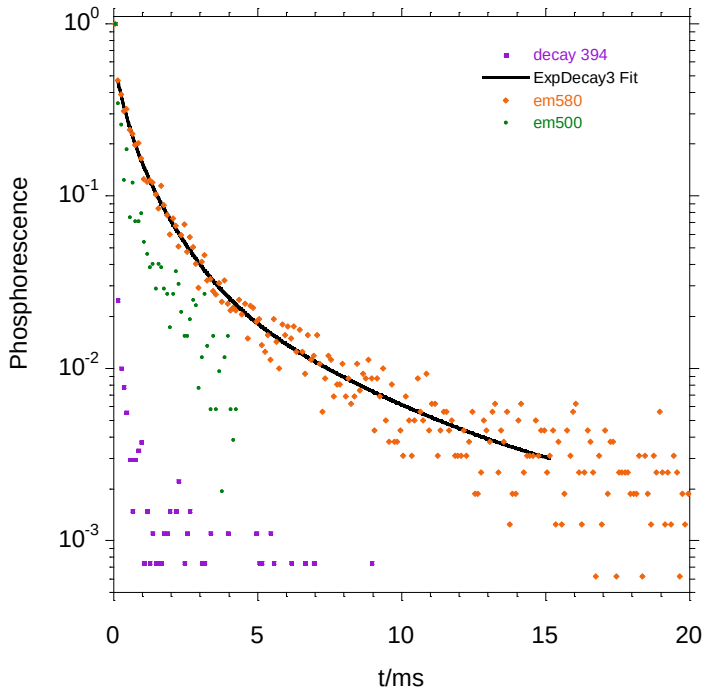


Figure S9. Phosphorescence decays of pristine 2D-C4/3D composite obtained by solution process. λ_{ex}= 300 nm, λ_{em}= 394 nm (pink), λ_{em}= 500 nm (green), λ_{em}= 580 nm (orange). Three-exponential fit $\sum_{i=1,3} Bi.exp(\frac{t}{Ti})$ of the 580 nm emission.

A1	t1	A2	t2	A3	t3	Adj. R-Square	<t> ms	τ_{av} ms
							1,07	2,25
0,22942	1,08811	0,19414	0,32889	4,14E-02	4,46789	0,99288		

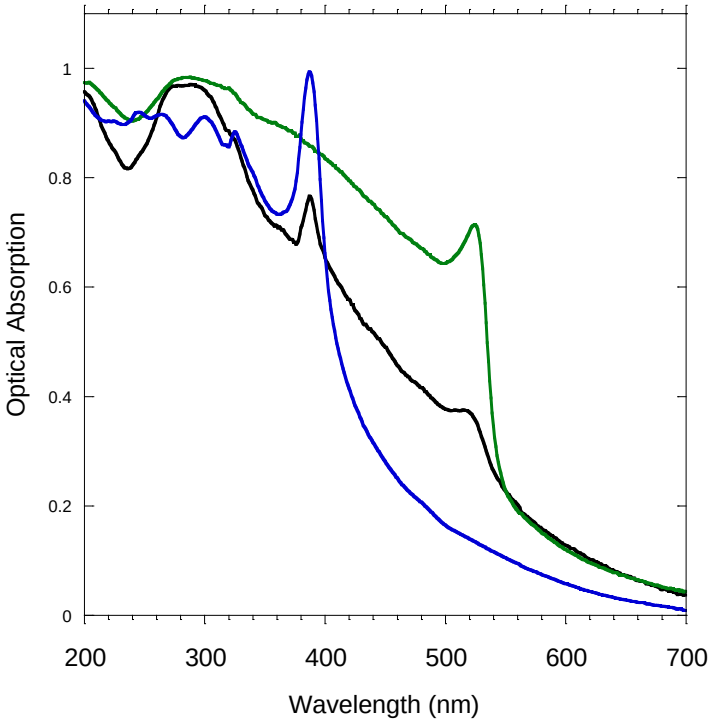
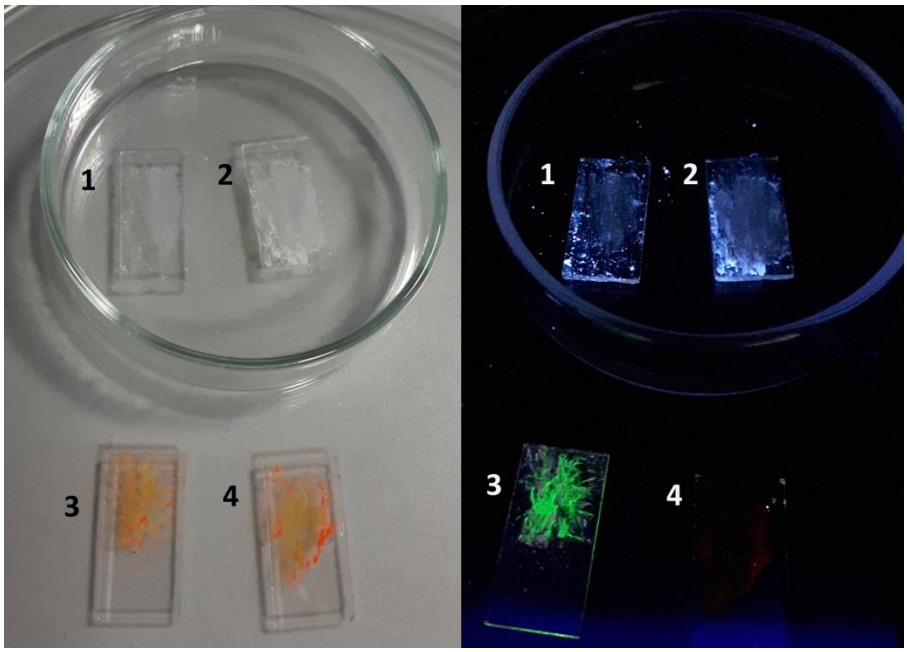


Figure S10. Optical absorption of crushed powders: 2D-C4 (blue line), 2D-C4/3D composite (black line), 3D (green line).



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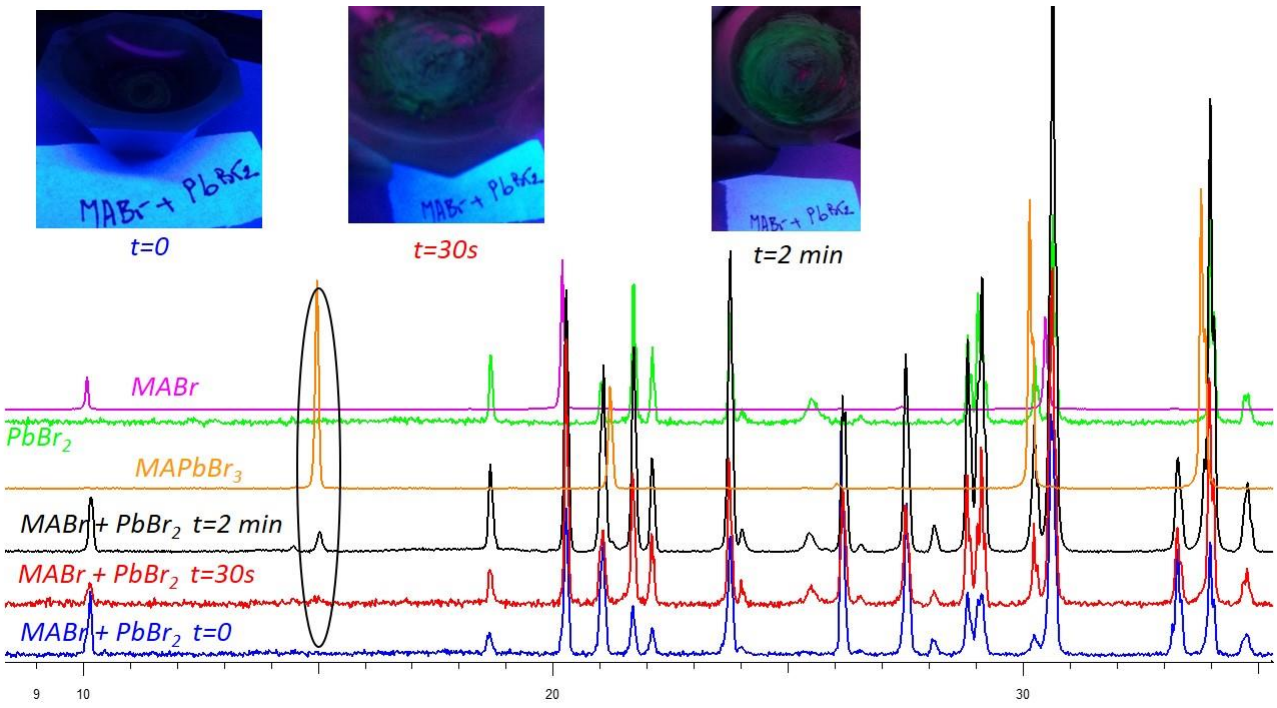


-b-

Figure S11 . a) Photos of crushed powders of 2D-C4 (1,2), 2D-C4/3D composite (3) and 3D (4) under ambient light (left) and UV light (right); b) Mechanical synthesis of a small quantity of $(CH_3NH_3)PbBr_3$ after 2 min crushing followed by XRPD (down) and photos under UV lamp (top) showing a slight green emission due to small size particles of $(CH_3NH_3)PbBr_3$.

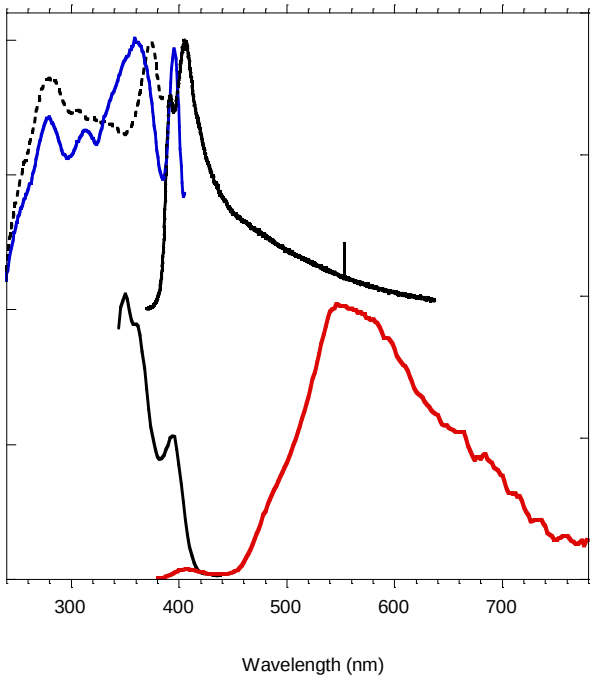
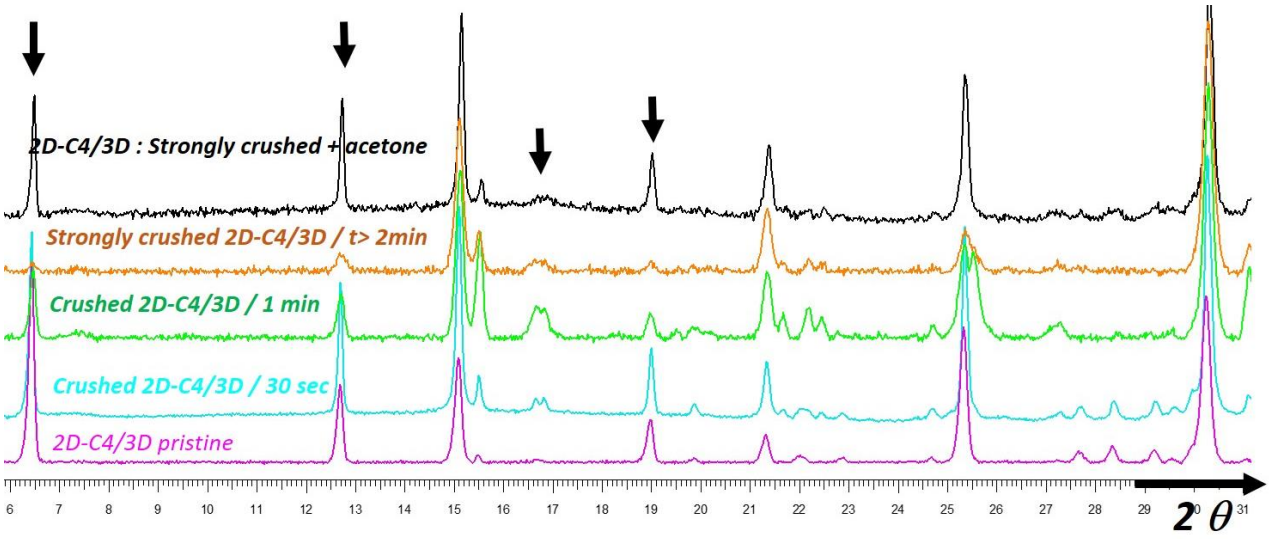


Figure S12 Emission properties of crystallized powder of $(GABA)_2PbBr_4$ (2D-C4) after strong grinding. PL (top, λ_{ex}= 310 nm, black solid line; λ_{em}=391 nm, black dotted line; λ_{em}=407 nm, blue solid line) and phosphorescence (bottom, λ_{ex}= 360 nm, red line; λ_{em}=550 nm, black line; delay 1ms, window 5 ms) spectra.



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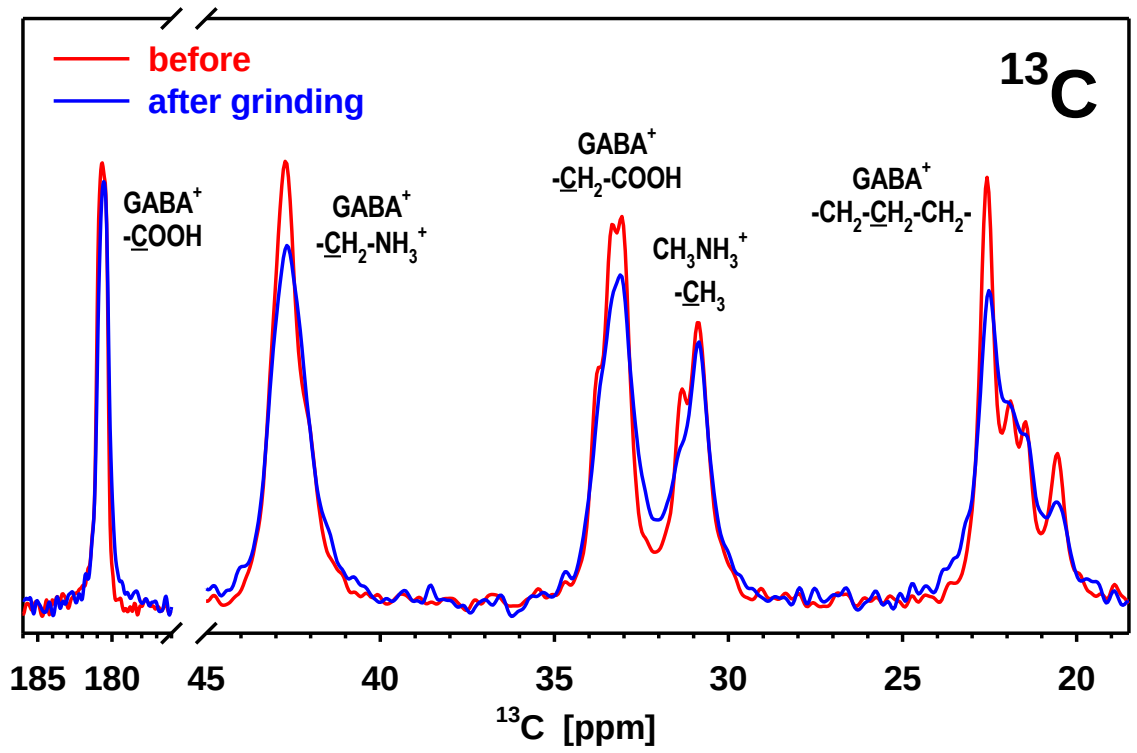


-b-

Figure S13 (a) XRPD of the 2D-C4/3D composite along with crushing time showing the amorphisation of the 2D component (broadening of corresponding lines as shown by some arrows), and XRPD of the ground composite after acetone treatment showing the recrystallization of the 2D component (narrowing of lines); b) solid state NMR of the 2D-C4/3D composite before (red) and after (blue) heavy grinding of the powder.

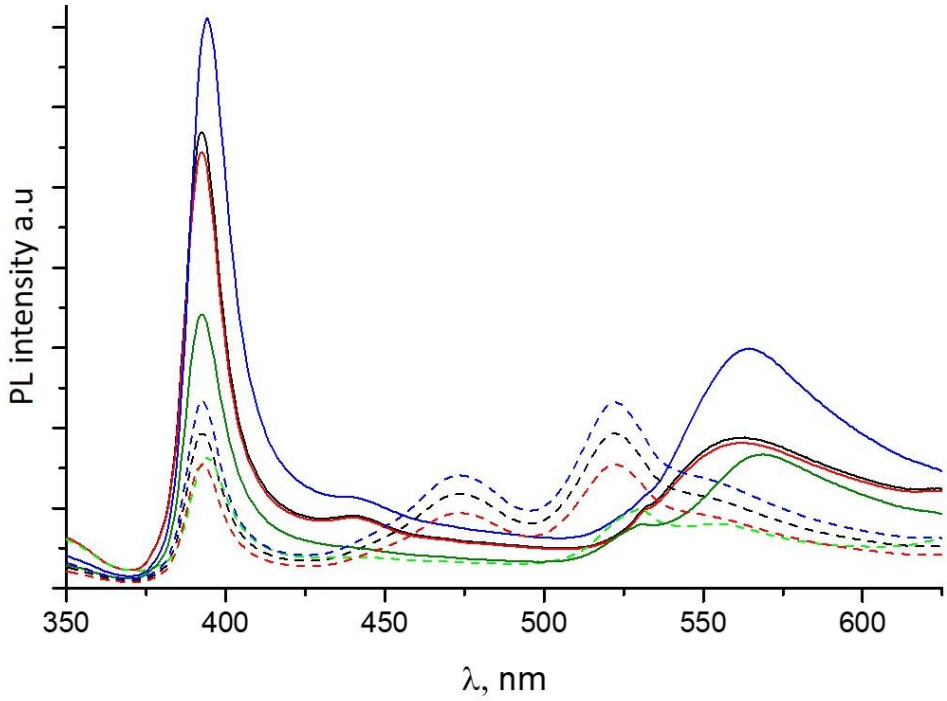


Figure S14. Reversible MCL process of a sample of the 2D-C4/3D(x2) composite : blue : cycle 1, black: cycle 2, red: cycle 3, green: cycle 4; dashed lines : crushed samples; full lines: pristine (blue line) and after acetone treatment.

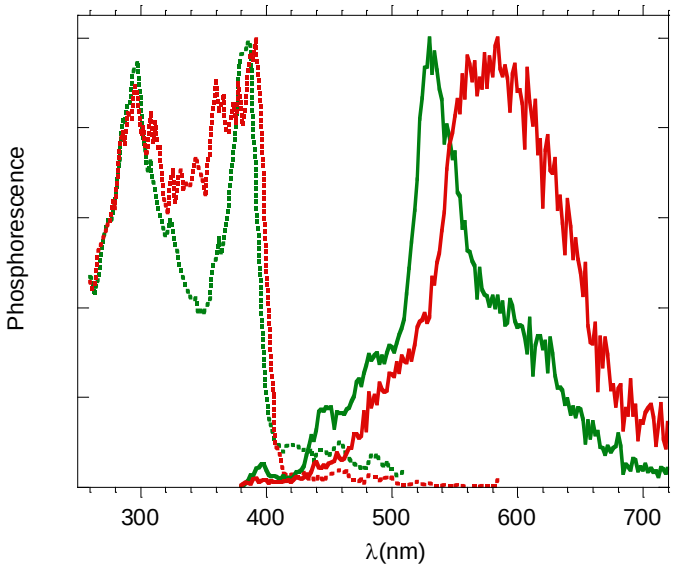
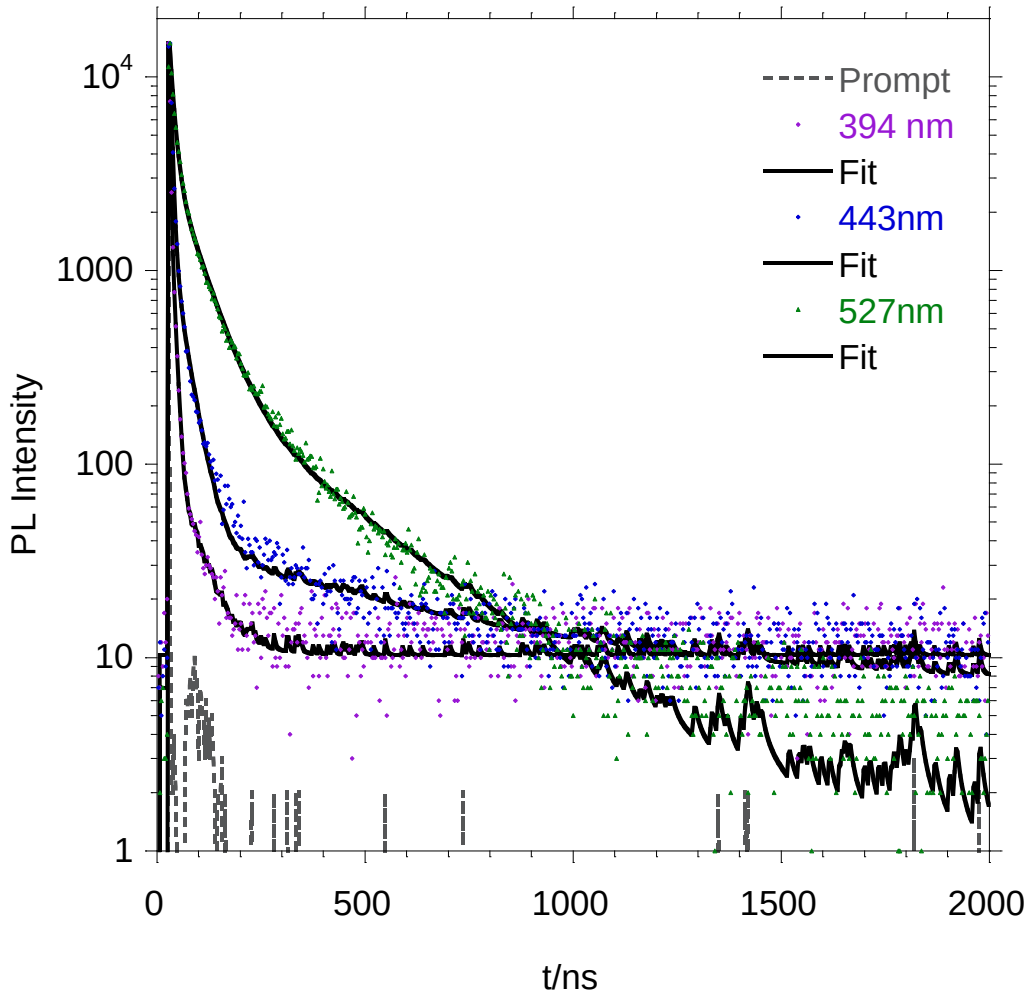


Figure S15. Phosphorescence emission of a crushed sample of 2D-C4/3D composite. (solid lines: green, delay 0.1 ms, window 0.2 ms; red, delay 1 ms, window 5 ms; λ_{ex} = 300 nm) and excitation spectra (dotted lines: green, delay 0.1 ms, window 0.2 ms; λ_{em} = 525 nm; red, delay 0.2 ms, window 0.5 ms; λ_{em} = 600 nm). Average lifetimes: emission at 560-620 nm (τ_{av} =1.9 ms) emission at 526 nm (τ_{av} =0.4 ms) .



	B1	B2	B3	T1	T2	T3	<t>/ns	τ_{av}	chisquare
em394	5,172513	0,302474	0,004065429	2,114356	8,772932	58,14513	2,52	5,69	1,14483
em443	0,131054	0,002015	2,733858	27,26704	568,5787	4,726384	6,15	45,89	1,41856
em527	1,184204	0,245021	0,0177888	10,26561	57,10298	280,0542	21,51	74,49	1,48370

Figure S16. PL decays of crushed 2D-C4/3D composite obtained by solution process. λ_{ex}= 300 nm, λ_{em}= 394 nm (pink), λ_{em}= 443 nm (blue), λ_{em}= 527 nm (green).Three-exponential fit $\sum_{i=1,3} Bi.exp(\frac{t}{Ti})$

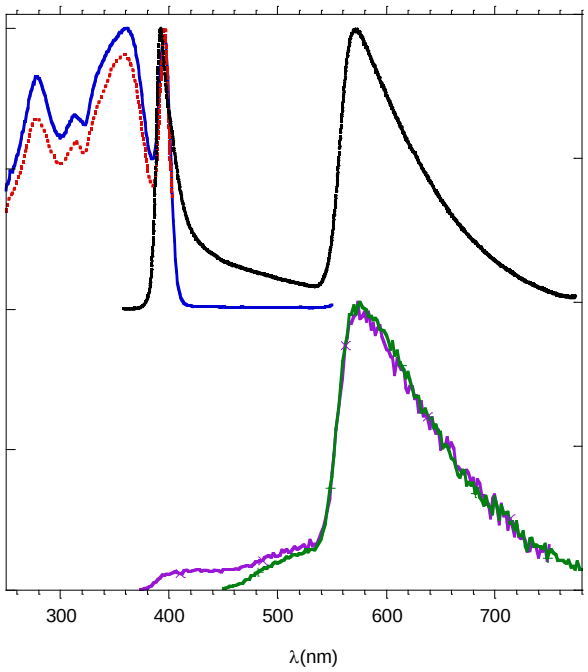


Figure S17. Emission properties of the 2D-C4/3D composite obtained by solid state process. Top: PL (λ_{ex}= 340 nm, black solid line; λ_{em}= 405 nm, red dashed line; λ_{em}= 570 nm, blue solid line. Bottom phosphorescence emission (solid lines: pink, delay 0.1 ms, window 2 ms, λ_{ex} = 280 nm; green, delay 0.2 ms, window 2 ms; λ_{ex} = 395 nm). Average lifetimes : emission at 580 nm (τ_{av} =2.5 ms).

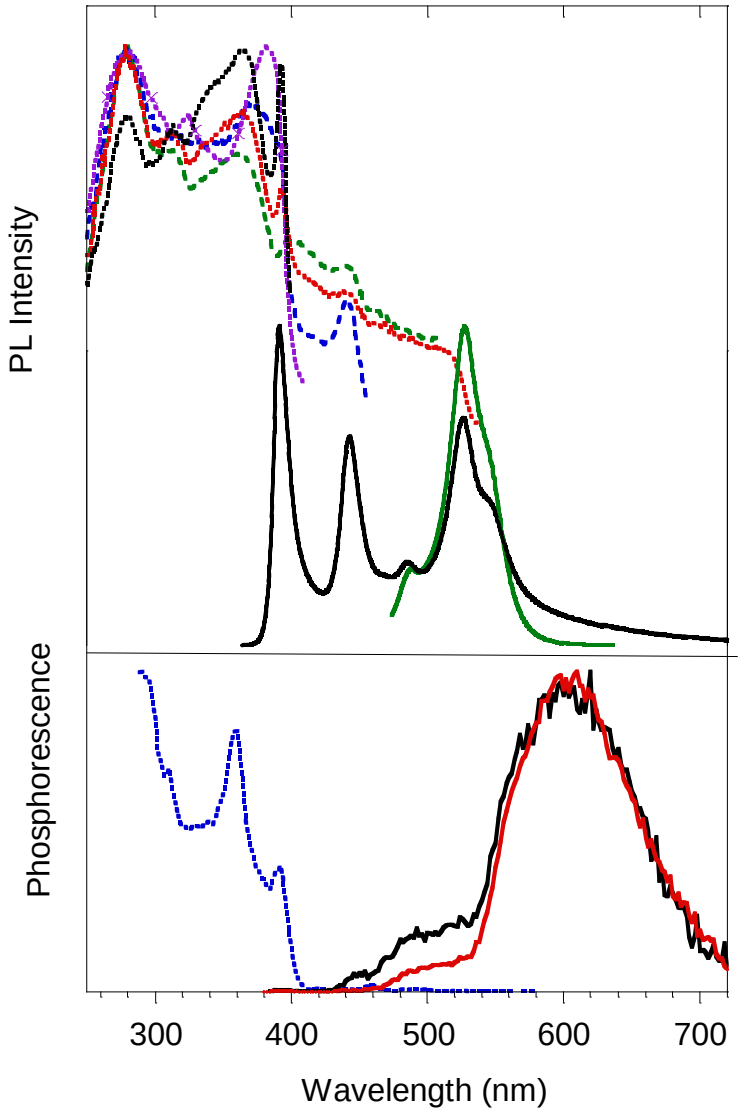


Figure S18 Emission properties of 2D-C4/3D composite, obtained by solid state process, after crushing with a spatula. PLE (dashed lines; λ_{em}= 405 nm, black; λ_{em}= 444 nm, pink; λ_{em}= 485nm, blue; λ_{em}= 527 nm, green; λ_{em}= 550nm, red) and PL spectra (λ_{ex}= 300 nm, black; λ_{ex}= 440 nm, green). Phosphorescence emission (λ_{ex}= 300 nm, delay 0.1 ms window 0.3 ms , black line, delay 0.2 ms, window 2 ms, red line) and excitation (λ_{em}= 620 nm, blue dashed line) spectra

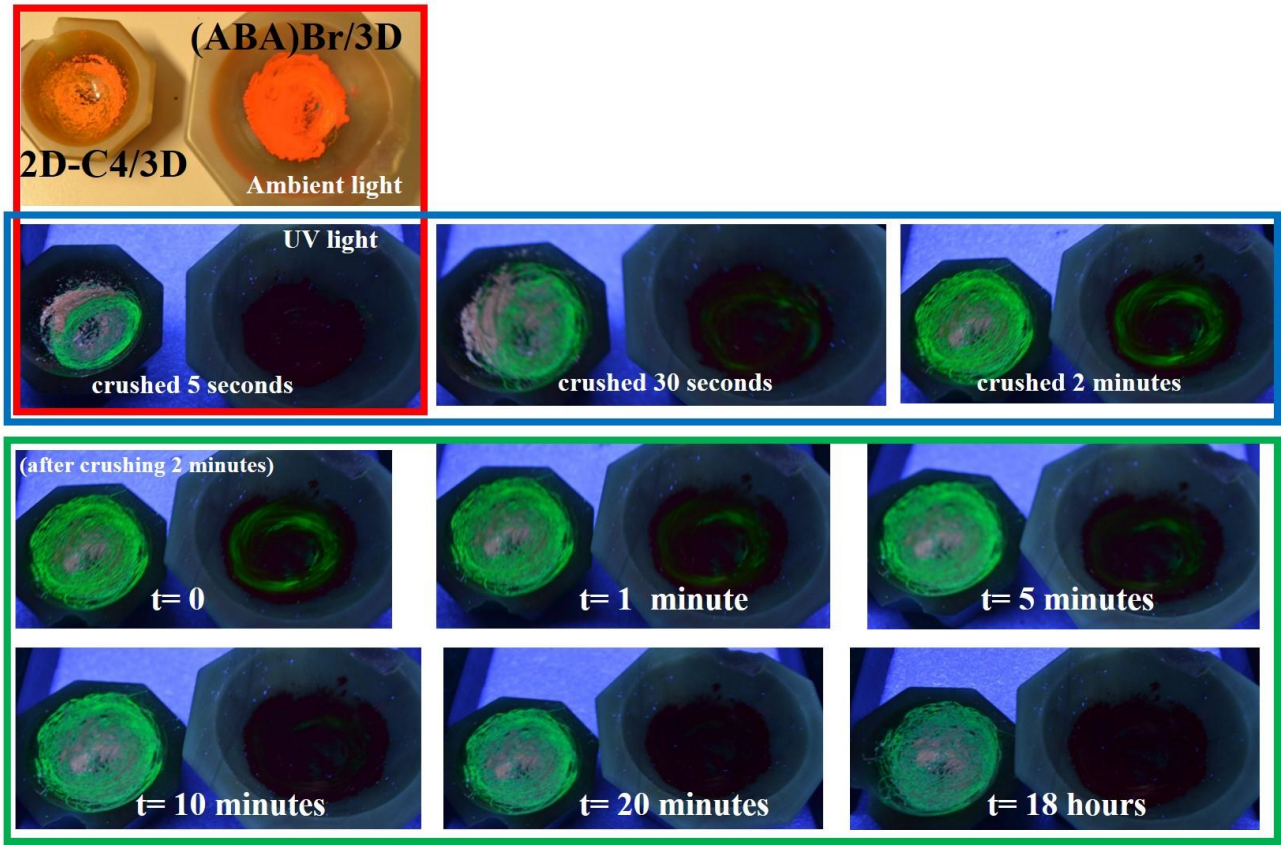


Figure S19 MCL properties of the 2D-C4/3D and (GABA)Br/3D composites : Ambient and UV light photos after 5 seconds crushing (red rectangle); UV-light photos after grinding, from 5 seconds to 2 minutes (blue rectangle); UV-light photos of samples crushed 2 minutes along with time (from t=0 to t=18 hours) (green rectangle).

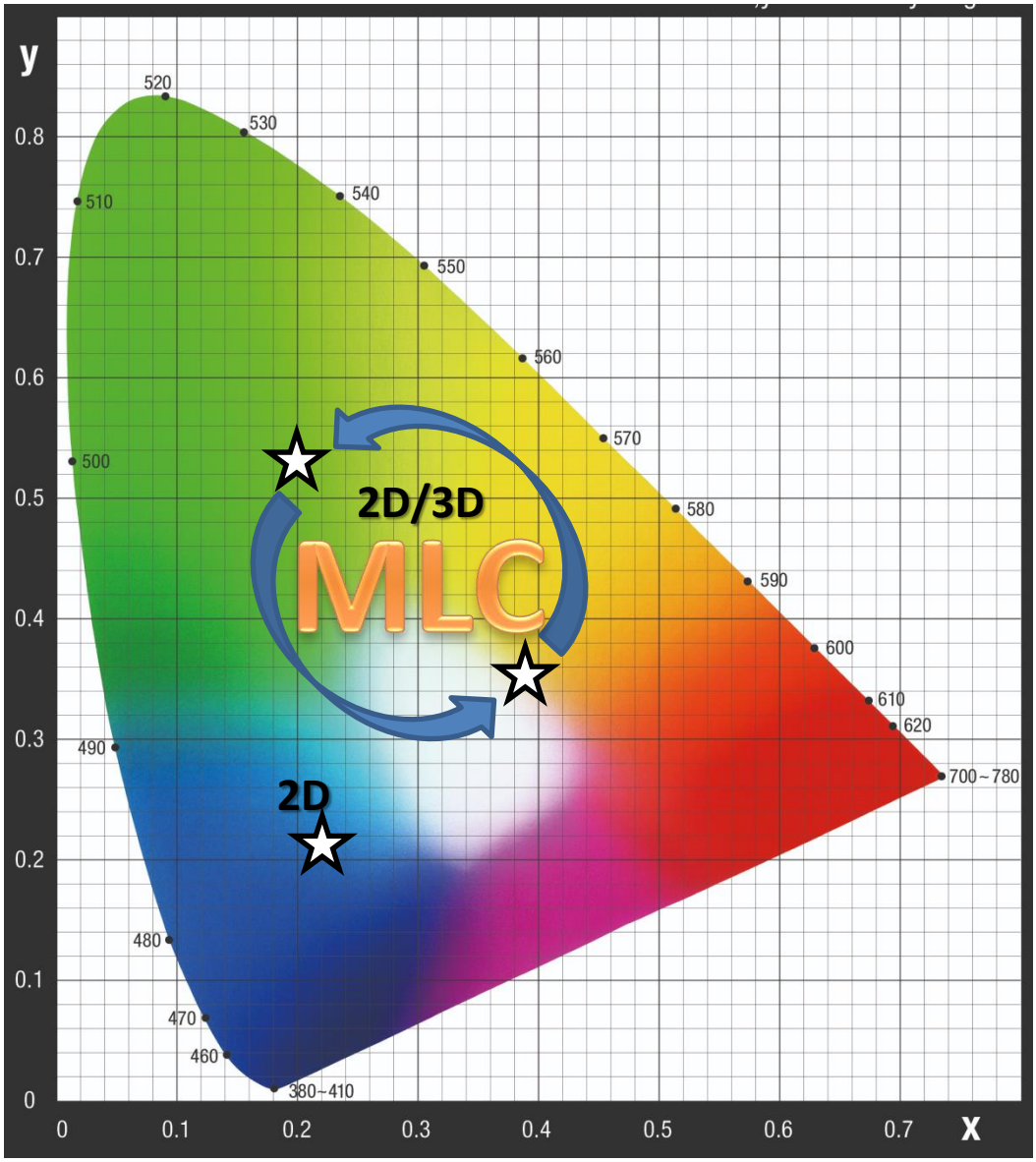


Figure S20 1931CIE chromaticity diagram coordinates of the 2D-C4 compound the of 2D-C4/3D composite and during MCL process.