

Supporting Information

Polymeric ionic liquid-based formulations for the fabrication of highly stable perovskite nanocrystal composites for photocatalytic applications

Sara Miralles-Comins,^a Marcileia Zanatta,^a Andrés F. Gualdrón-Reyes,^{a,b} Jhonatan Rodriguez-Pereira,^{c,d} Iván Mora-Seró,^{a*} Víctor Sans^{a*}

^a Institute of Advanced Materials (INAM), Universitat Jaume I (UJI), Avenida de Vicent Sos Baynat, s/n, 12071 Castelló de la Plana, Castellón, Spain.

^b Facultad de Ciencias, Instituto de Ciencias Químicas, Isla Teja, Universidad Austral de Chile, 5090000, Valdivia, Chile.

^c Center of Materials and Nanotechnologies, Faculty of Chemical Technology, University of Pardubice, Nam. Cs. Legii 565, 53002 Pardubice, Czech Republic.

^d Central European Institute of Technology, Brno University of Technology, Purkyňova 123, 612 00 Brno, Czech Republic.

* sans@uji.es; sero@uji.es

Table of Contents

1. Experimental Section.....	2
1.1 Synthesis of the monomeric ionic liquids	2
1.2. Synthesis of CsPbX ₃ (X = Br and Cl:Br combinations)	2
1.3 General characterization	3
1.3.1 Characterization of AcrEMA-TFSI	3
1.3.2 Characterization of the films	6
2. Optimization of formulation.....	9
3. Stability Tests.....	11
4. Application.....	13
5. References.....	17

1. Experimental Section

1.1 Synthesis of the monomeric ionic liquids

[2-(acryloyloxy)ethyl]trimethyl-ammonium chloride (**AcrEMA-Cl**) was purchased from Sigma Aldrich and used as starting reagent for synthesizing **AcrEMA-N(CN)₂**, **AcrEMA-BF₄**, **AcrEMA-TFSI** by anion exchange reaction, without further purification. In the case of using **AcrEMA-Cl** as mL, it was necessary to evaporate the water since the commercial product contain 20 wt% of water.

[2-(acryloyloxy)ethyl]trimethyl-ammonium iodide (**AcrEMA-I**) was synthesized according to a procedure described elsewhere.¹

[2-(acryloyloxy)ethyl]trimethyl-ammonium dicyanamide (**AcrEMA-N(CN)₂**), [2-(acryloyloxy)ethyl]trimethyl-ammonium tetrafluoroborate (**AcrEMA-BF₄**), [2-(acryloyloxy)ethyl]trimethyl-ammonium bis(trifluoromethane)sulfonimide (**AcrEMA-TFSI**) were synthesized from commercial **AcrEMA-Cl** by an anion exchange with silver dicyanamide, sodium tetrafluoroborate and lithium bis(trifluoromethane)sulfonimide, respectively, according to a similar protocol reported.² **AcrEMA-TFSI** synthesis is fully detailed. LiNTf₂ (42.7g, 148 mmol) was dissolved in water (40 mL) and it was added dropwise to an aqueous solution (40 mL) of [2-(acryloyloxy)ethyl]trimethyl-ammonium chloride (24 g, 124 mmol). The mixture formed two liquid phases and it was stirred rapidly for 18 h at room temperature. The phases were then separated and the aqueous phase was extracted three times with dichloromethane (100 mL). The combined organic phases were washed three times with water (125 mL) and dried over MgSO₄ anhydride. The product was further dried under reduced pressure at 45 °C for 3 h. The yield was 91 % (49.5 g).

1.2. Synthesis of CsPbX₃ (X = Br and Cl:Br combinations)

CsPbX₃ PNCs were prepared by a hot-injection method by mixing both the Cs-oleate and PbX₂ solutions in stoichiometric amounts with some modifications. To prepare the Cs-oleate solution, 0.407 g Cs₂CO₃ (202126, 99.9 %, Sigma-Aldrich), 1.5 mL oleic acid (OA, 364525, 90 %, Sigma-Aldrich) and 20 mL of 1-octadecene (1-ODE, O806, 90 %, Sigma-Aldrich) were mixed into a 50 mL-three neck flask, under vacuum for 30 min at 80 °C under vigorous stirring. The temperature was increased to 120 °C and kept under vacuum for 30 min. The mixture was heated at 150 °C under N₂ atmosphere, until complete Cs₂CO₃ dissolution. The resultant transparent solution was kept at 120 °C before use.

For the synthesis of CsPbBr₃ and CsPbCl_{3-x}Br_x 0.8 g PbBr₂ (abcr; AB202085, 99.998%) and the corresponding Cl:Br molar ratios (3:1 and 1:1) (PbCl₂, abcr, AB202087, 99.999%, ABCR) were mixed with 50 mL 1-ODE into a 100 mL-three neck flask and degasified at 120 °C for 1 h under stirring. Then, 5.0 mL of each preheated OA and oleylamine (HT-OA100, 98 %, Sigma-Aldrich) were added to the flask to promote the PbX₂ dissolution.

Then, the temperature of PbX_2 mixture was rapidly increased to reach $180\text{ }^\circ\text{C}$ and 4 mL of preheated Cs-oleate was swiftly injected, obtaining a green precipitate in the colloidal solution. The flask was immediately added into an ice bath for 5 s to quench the reaction mixture. To isolate the final product, PNCs are centrifuged at 5000 for 5 min with methyl acetate (MeOAc, 296996, 99.5%, Sigma Aldrich) (30 mL of PNCs liquor washed with 60 mL MeOAc). The supernatant is discarded, the PNCs pellets are redispersed in hexane (CHROMASOLV, 34859, 99.7 %, Honeywell) at a concentration $\sim 60\text{ mgmL}^{-1}$ and stored in the fridge for 24 h.

1.3 General characterization

1.3.1 Characterization of AcrEMA-TFSI

Elemental Analysis: Calculated (%): C, 27.40; H, 3.68; N, 6.39; S, 14.63; Found (%): C, 26.53; H, 3.68; N, 6.66; S, 14.70.

^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ / ppm = 6.40 (dd, 1H), 6.22 (dd, 1H), 5.99 (dd, 1H), 4.75 (m, 2H), 4.03 (m, 2H), 3.50 (s, 9H)

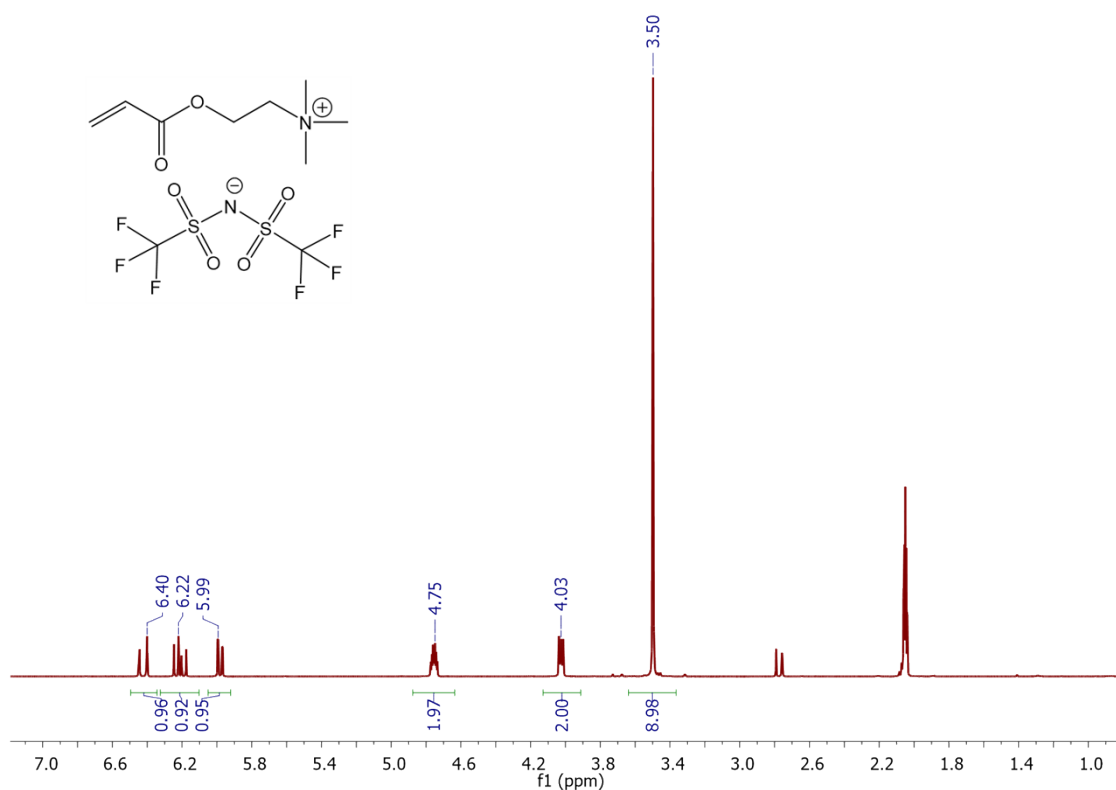


Figure S1. ^1H NMR (400 MHz) spectra of AcrEMA-TFSI in $(\text{CD}_3)_2\text{CO}$

^{13}C NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ / ppm = 165.7, 132.6, 128.8, 122.8 (q, CF_3), 66.0, 59.0, 54.8

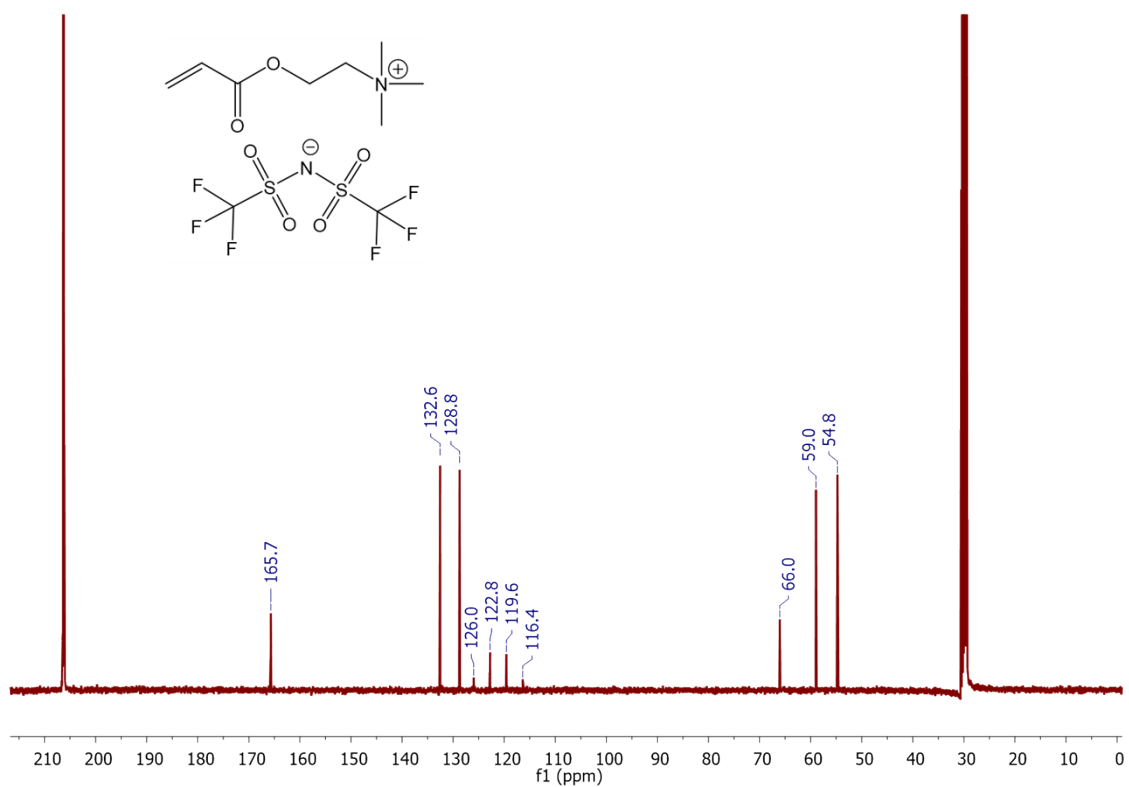


Figure S2. ^{13}C NMR (400 MHz) spectra of AcrEMA-TFSI in $(\text{CD}_3)_2\text{CO}$



SMC-P99, scan neg, MeOH, 20V, rango 30-600

TQD_VS_0017C 1 (0.170)

Scan ES-
4.85e7

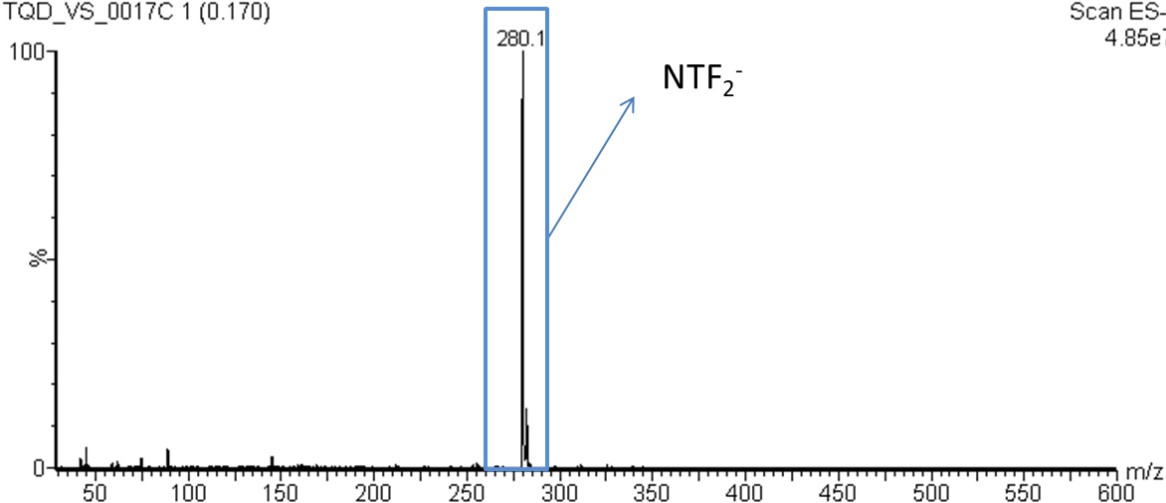


Figure S3. ESI-MS spectra of AcrEMA-TFSI in positive mode (up) and negative mode (down)

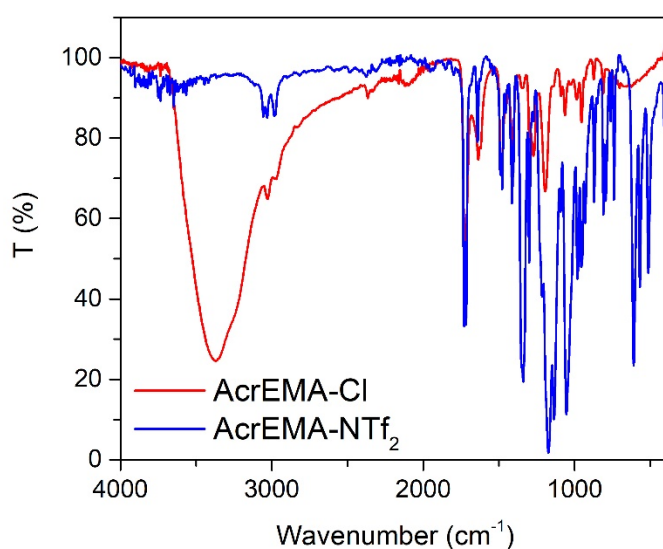


Figure S4. FT-IR spectra of AcrEMA-Cl (red) and AcrEMA-TFSI (blue). Disappearance of the chloride band after the anion exchange reaction with LiNTf₂, showing that the reaction was completed

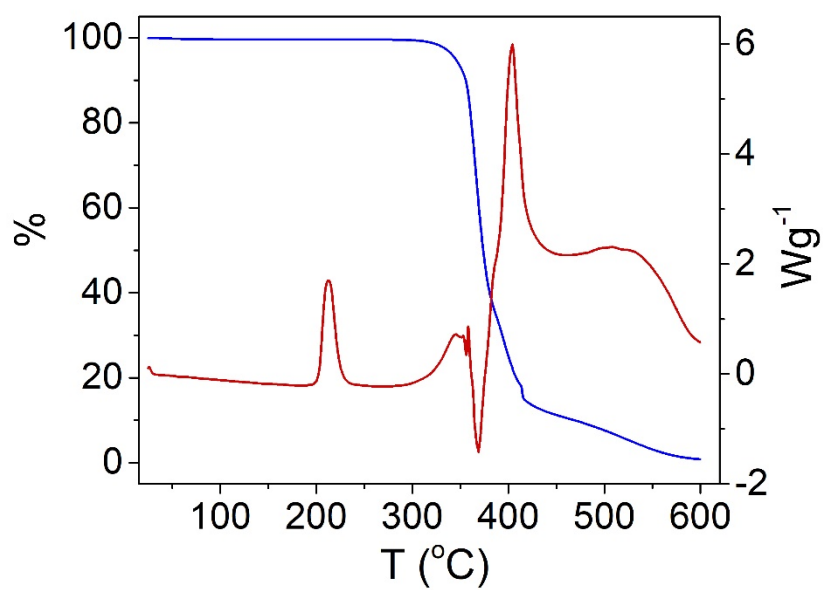


Figure S5. DSC-TGA spectra of AcrEMA-TFSI

1.3.2 Characterization of the films

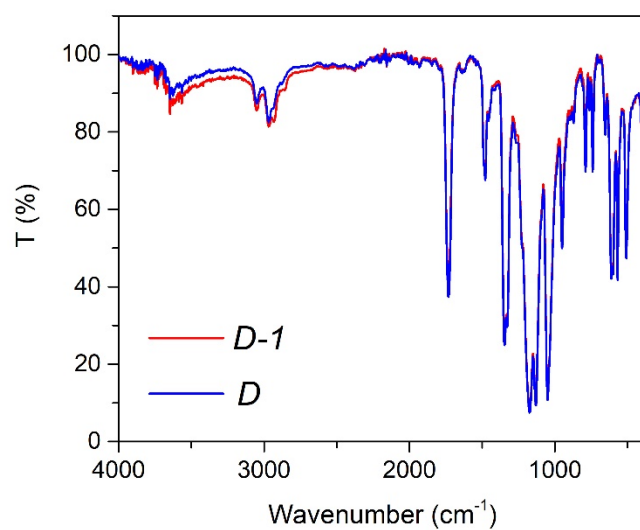


Figure S6. FT-IR spectra of a film *D* (blue) and *D-1* film (red)

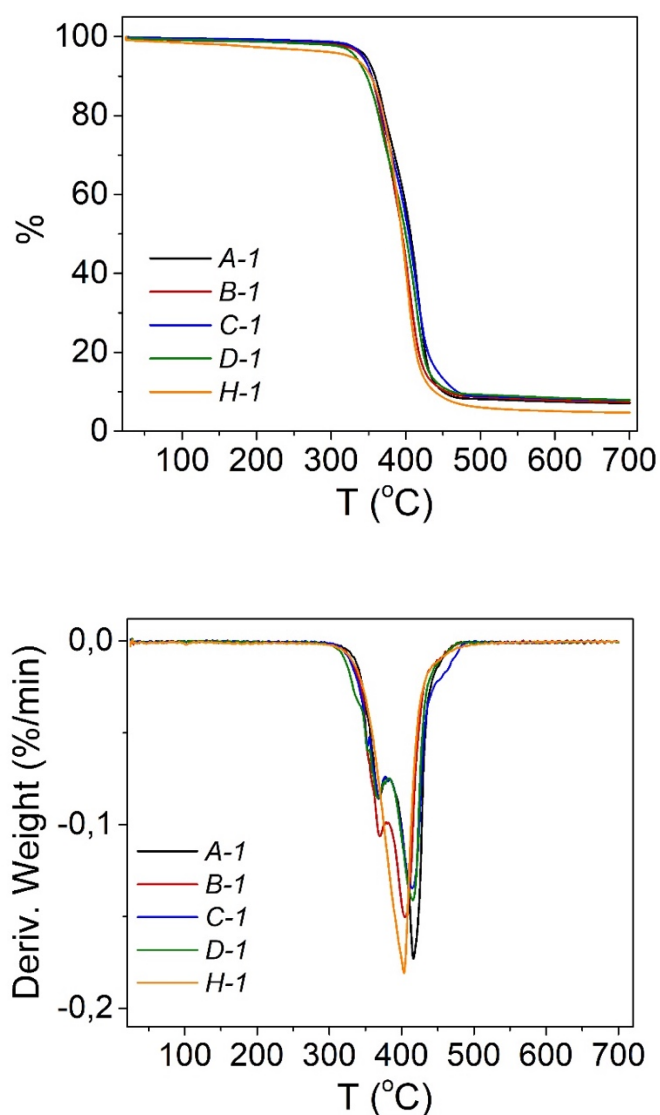


Figure S7. TGA spectra (up) and the DTG spectra (down) of all the different **PILX@PS1** formulations capable to stabilize CsPbBr₃

Table S1. Summary of the T_{onset} obtained from the above TGA spectra for the different formulations evaluated and the monomeric ionic liquid (AcrEMA-TFSI)

Formulation	T_{onset} (°C)
A-1	385
B-1	369
C-1	373
D-1	372
D	387
H-1	375
AcrEMA-TFSI	361

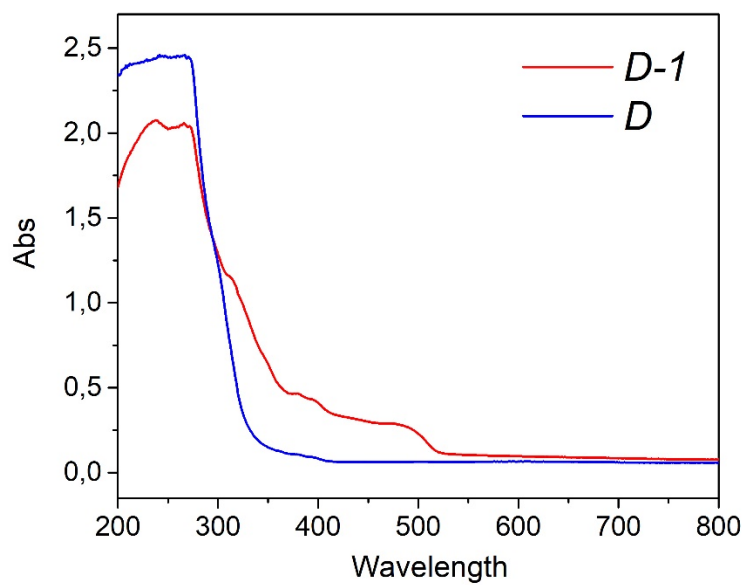


Figure S8. Absorbance spectra of *D* (blue) and *D-1* (red)

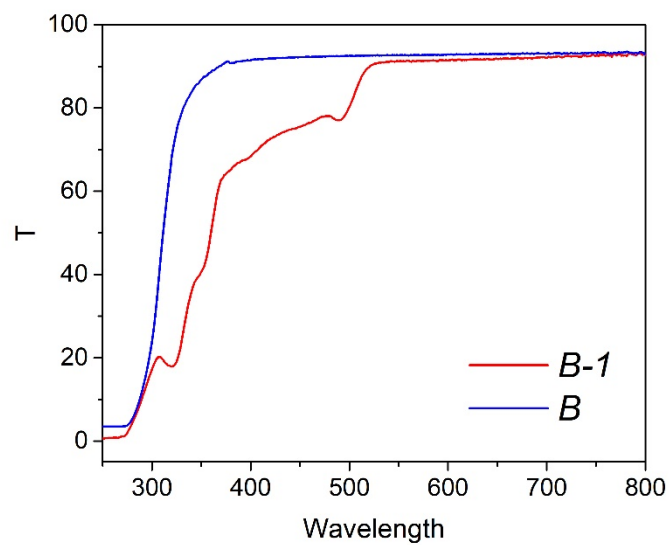


Figure S9. Transmittance spectra of *B* (blue) and *B-1* (red)

2. Optimization of formulation

Table S2. Summary of monomers employed and their capacity to form a film and to stabilize the *PS1* after polymerization

Entry	Monomeric Ionic Liquids	Observations	Film Formation	Film Photoluminescence
1	AcrEMA-Cl	Insoluble monomer	X	X
2	AcrEMA-I	Insoluble monomer	X	X
3	AcrEMA-N(CN) ₂	Soluble monomer	V	X
4	AcrEMA-BF ₄	Insoluble monomer	X	X
5	AcrEMA-TFSI	Soluble monomer	V	V

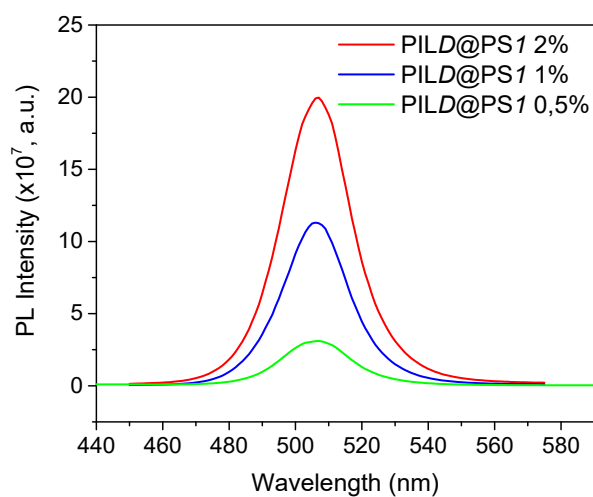
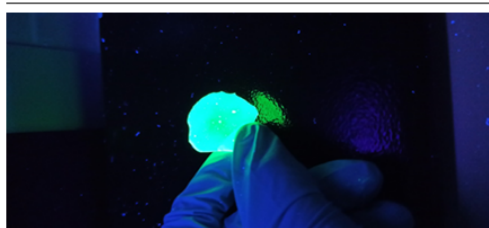
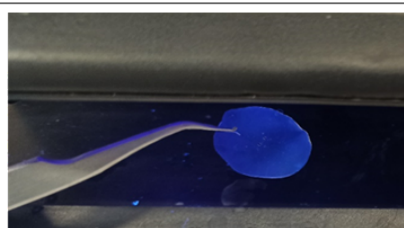


Figure S10. Photoluminescence (PL) spectra of **PILD@PS1** films using different perovskite concentrations (2 wt%, 1 wt%, 0.5 wt%)

Perovskites	PILA		PILB		Pure PNCs	
	PLQY	nm	PLQY	nm	PLQY	nm
CsPbBr_3	50	512	45	510	80	505
$\text{CsPbBr}_{1.5}\text{Cl}_{1.5}$	1,5	448	1,2	450	4	458
$\text{CsPbBr}_{0.75}\text{Cl}_{2.25}$	1,2	413	1,4	413	6	436



CsPbBr_3



$\text{CsPbCl}_{1.5}\text{Br}_{1.5}$



$\text{CsPbCl}_{2.25}\text{Br}_{0.75}$

Figure S11. Summary of the PLQY and wavelength (in nm) of the different perovskites embedded with two different formulations (**PILA** and **PILB**), see **Figure 1B**, and without embedding (Pure PNCs). And their respective film colours

3. Stability Tests

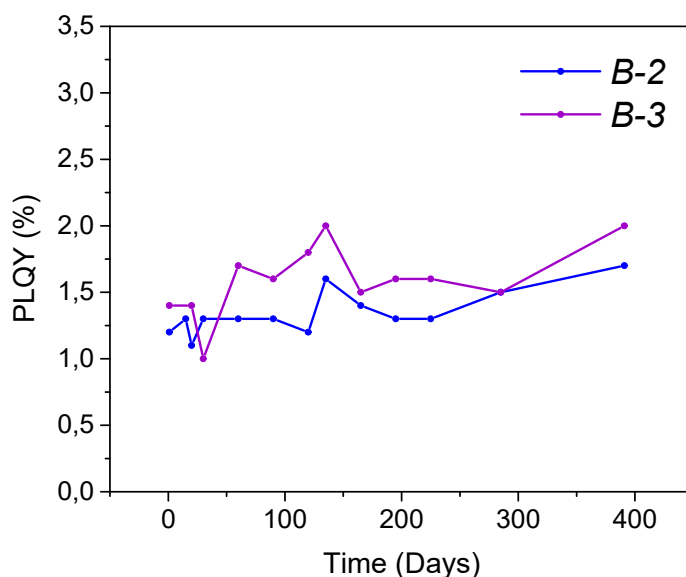


Figure S12. Stability study in the dark measuring the photoluminescence quantum yield (PLQY) along more than 400 days for $\text{CsPbCl}_{1.5}\text{Br}_{1.5}$ ($Y=2$) and $\text{CsPbCl}_{2.25}\text{Br}_{0.75}$ ($Y=3$) encapsulated into **PILB** formulation

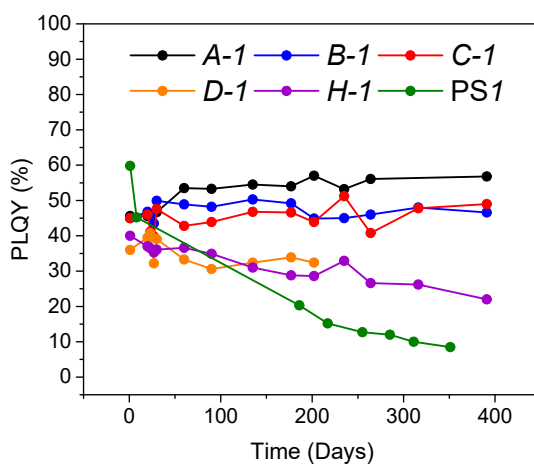


Figure S13. Stability study in the dark measuring the PLQY along more than 400 days using all the formulations capable to stabilize CsPbBr_3 . **PILA**, **PILB** and **PILC** are the best formulation for stabilizing PNCs, keeping the PLQY of the films around 50 and 60%. On the contrary, the PLQY of not embedded **PS1** decreases 70% in less than 200 days. However, not all the polymeric matrices are good for stabilizing CsPbBr_3 since **PILD** and **PILH** lost partially and even totally their photoluminescence after some time.

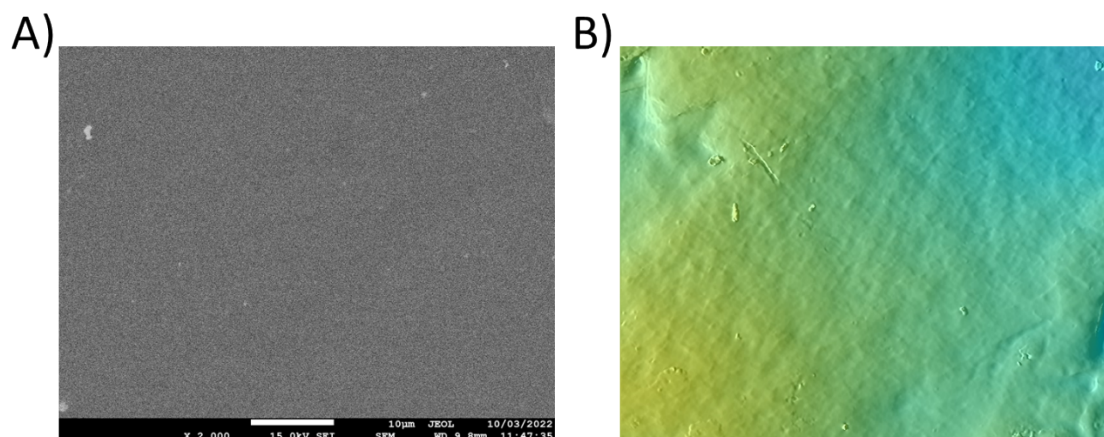


Figure S14. Images of a **B-1** film obtained by **A)** SEM, and **B)** profilometry

Table S3. Chemical atomic composition of pristine CsPbBr₃ PNCs and **B-1** samples

Perovskite	C (at.%)	O (at.%)	Pb (at.%)	Br (at.%)	Cs (at.%)	N (at.%)	F (at.%)	S (at.%)	Cs/Pb	Br/Pb
Pristine PNCs	73.85	20.34	1.03	2.69	0.64	1.45	-	-	0.62	2.61
B-1	57.61	18.67	0.03	0.06	0.03	5.55	12.84	5.21	1.00	2.00

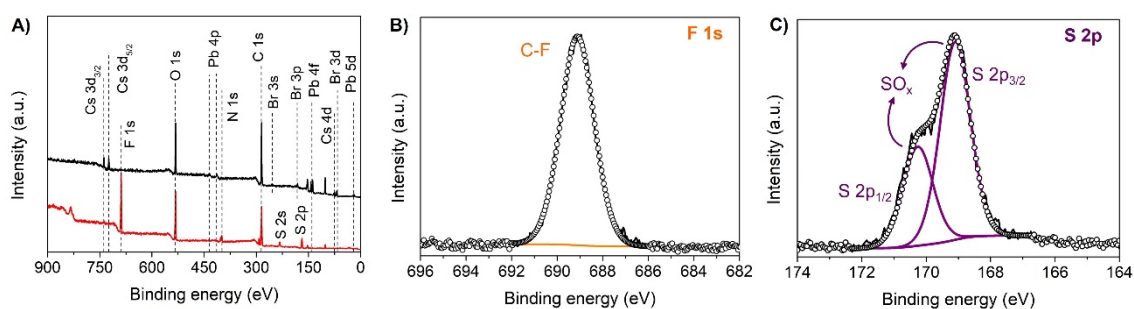


Figure S15. **A)** XPS survey and HR-XPS; **B)** F 1s; and **C)** S 2p spectra for pristine CsPbBr₃ PNCs and **B-1** samples

4. Application

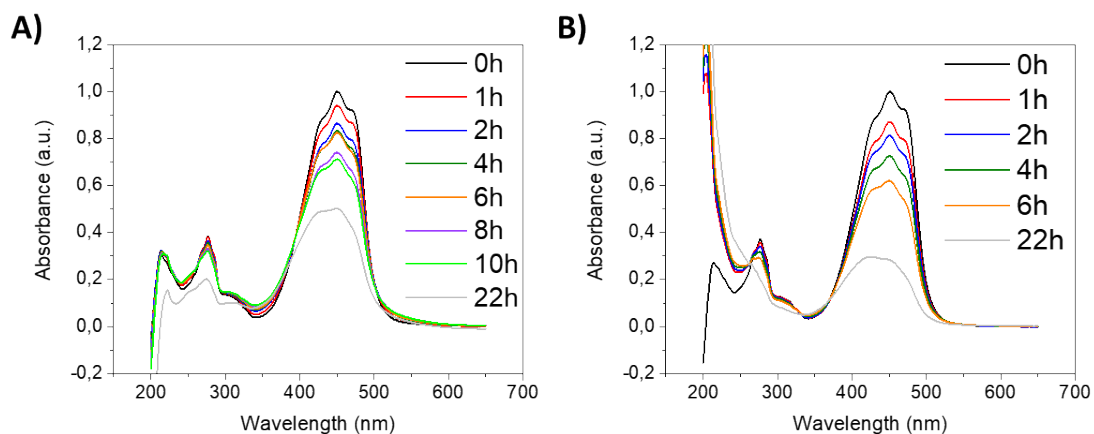
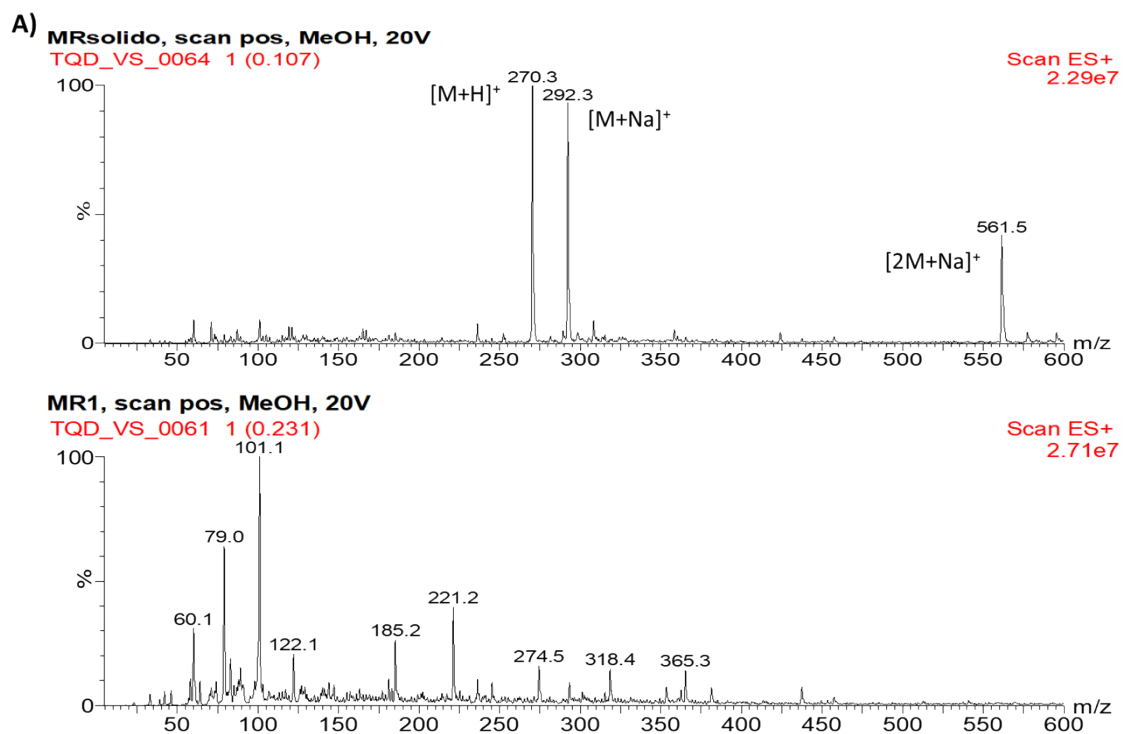


Figure S16. UV-Vis spectra during methyl red degradation under visible light **A)** control experiment (Blank); **B)** using **PILB** film



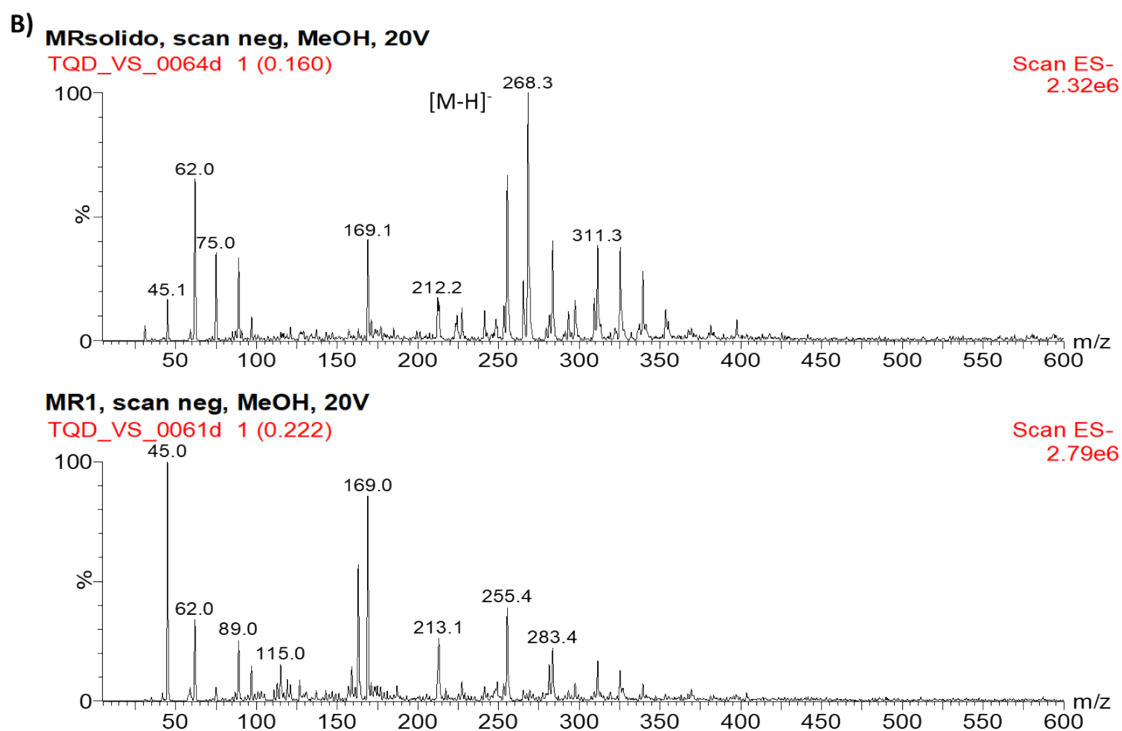


Figure S17. ESI-MS spectra of pure methyl red (MRsolido) and MR after photodegradation (MR1) using **B-1** film as photocatalyst. The representative peaks of MR disappeared, appearing new peaks **A)** in positive mode; **B)** in negative mode

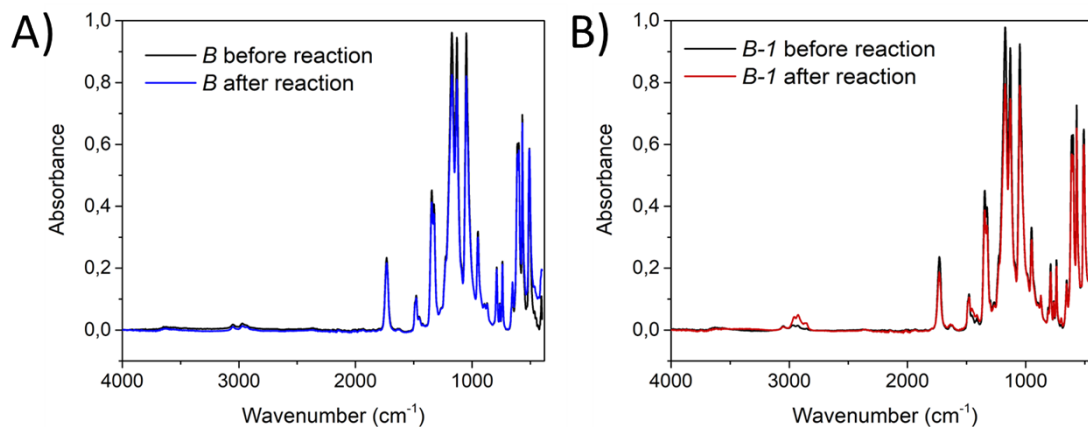


Figure S18. FT-IR spectra before and after photocatalysis reaction of **A)** a **B** film and, **B)** a **B-1** film



Figure S19. Colour of the films **B-1** (left) and **B** (right) after the third cycle

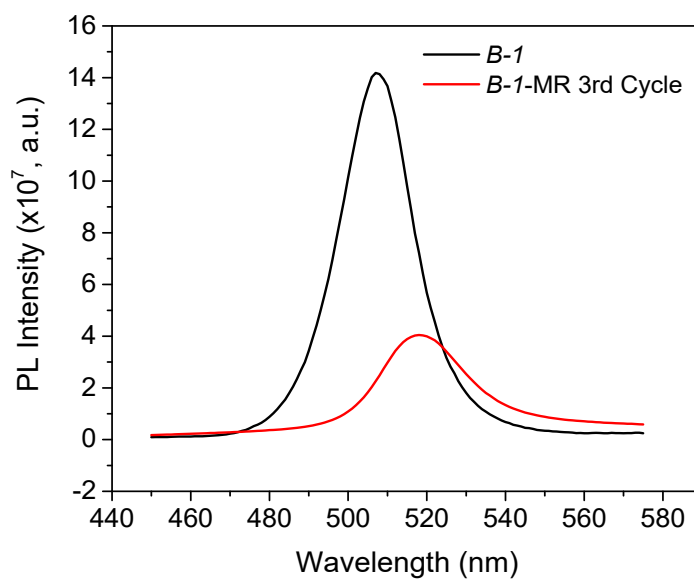


Figure S20. Photoluminescence spectra of initial **B-1** film and after 3 cycles of 22h immersed into a solution of MR and illuminated with visible light

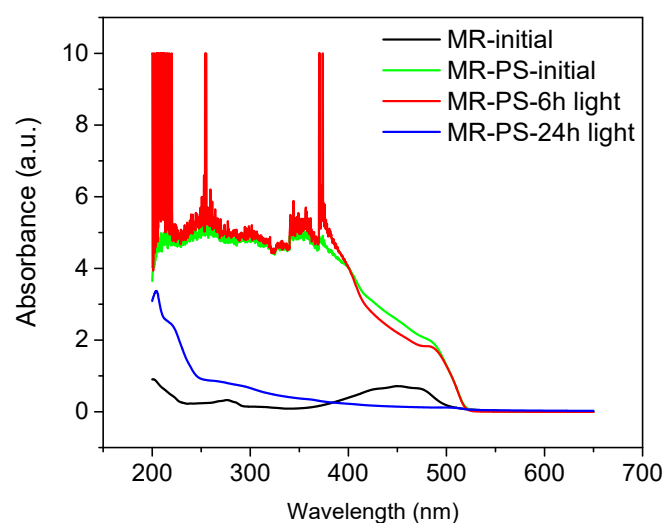


Figure S21. The absorption spectra during MR photodegradation after introducing pristine CsPbBr₃ dissolved in hexane as photocatalyst illuminating 22h with visible light. The methyl red solution (MR-initial) was measured neat (before adding PNCs) and after adding the PNCs (MR-PS-initial). After 22h, not only MR but also the PNCs signal disappeared

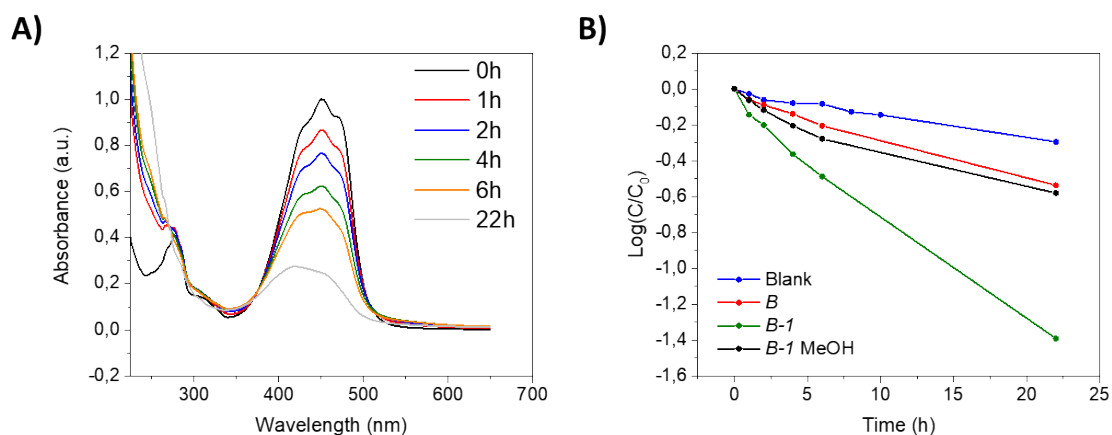


Figure S22. A) UV-Vis spectra showing the MR photodegradation using **B-1** film and a hole scavenger (MeOH) during 22h illuminating with visible light; **B)** Comparison of the kinetics of the blank, **B**, **B-1** and **B-1** with a hole scavenger (MeOH). The graphic shows that using a hole scavenger, **B-1** film have same behaviour as **B** film. Therefore, the PNCs are not involving in the process, the perovskite photodegradation is being blocked by MeOH

5. References

1. Ngulube, R.; Oderinde, O.; Kalulu, M.; Pan, R.; Ejeromedoghene, O.; Li, N.; Zhou, J., Designing a robust recyclable tricopolymer poly(ionic liquid) macroligand for copper-mediated atom transfer radical polymerization in non-aqueous biphasic systems. *New Journal of Chemistry* **2020**, *44* (3), 861-869.
2. Wales, D. J.; Cao, Q.; Kastner, K.; Karjalainen, E.; Newton, G. N.; Sans, V., 3D-Printable Photochromic Molecular Materials for Reversible Information Storage. *Adv Mater* **2018**, *30* (26), 1800159.