

Ligand and environment dependence of the spontaneous and stimulated emission properties of fully inorganic CsPbBr₃ perovskite nanocrystals

S.Milanese¹, M. L. De Giorgi¹, G. Morello², M. I. Bodnarchuk³, M. Anni¹

¹ Dipartimento di Matematica e Fisica “Ennio De Giorgi”, Università del Salento, 73100

² Unit of Lecce, CNR IMM Institute for Microelectronics and Microsystems, 73100 Lecce, Italy

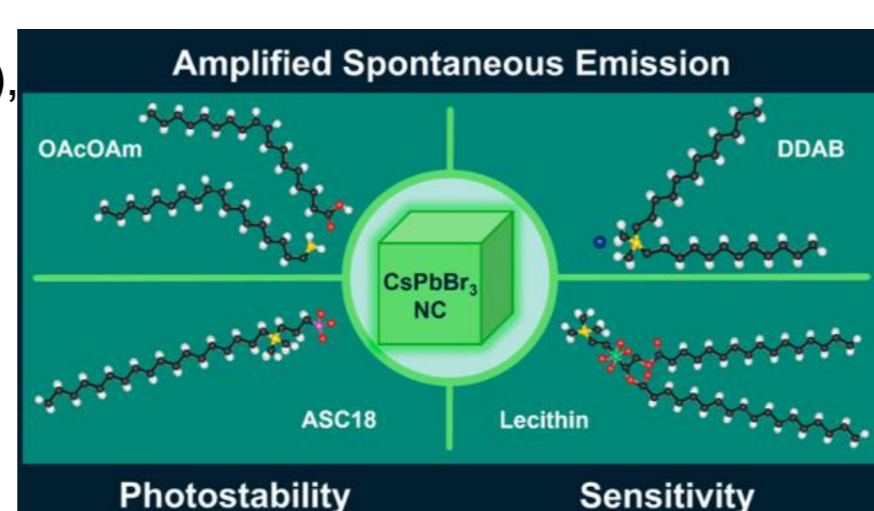
³ Institute of Inorganic Chemistry, Department of Chemistry and Applied Bioscience, ETH Zürich, CH-8093 Zürich, Switzerland

INTRODUCTION & AIM

All inorganic lead halide perovskite nanocrystals (NCs), and in particular CsPbBr₃ NCs, are emerging as promising active materials for light emitting devices, like LEDs and lasers.

One of the key parameters to synthesize robust and stable NCs is the choice of surface ligands, that are fundamental in determining the size and shape of the NCs and a proper surface passivation.

Despite this, a systematic investigation of the ligand role on the spontaneous and on the Amplified Spontaneous Emission (ASE) properties of perovskite NCs is still missing. In this work we aim to fill this gap, providing a complete investigation of the emission properties of perovskite NCs with four different capping ligands, namely oleic acid and Oleylamine, didodecyltrimethylammonium bromide (DDAB), 3-(*N,N*-dimethyloctadecylammonio)-propanesulfonate (ASC18) and lecithin.



METHOD

Thin-Film Deposition. Thin films have been deposited by spin coating (@600 rpm) the NC solution on quartz substrates at room temperature under chemical hood.

Thin-Film Characterization. ASE measurements were performed by exciting the samples with an LBT MNL100 Nitrogen laser (3 ns pulses @ 337 nm), focused onto the sample surface in a rectangular stripe (4 mm length and 80 μ m width) in edge-pump configuration. The emission was collected from the edge of the sample, dispersed by a 0.75 m focal length spectrograph (Acton 750), and analyzed by an Andor air-cooled Si CCD. The spectral resolution was 0.5 nm.

The experiments were carried out at room temperature by placing the samples in a vacuum chamber and using two pressure levels: 10⁻¹ mbar (named *vacuum*) and atmospheric pressure (named *air*).

The PLQY measurements have been performed by exciting the films inside a 3P-GPS-060 Labsphere integrating sphere, with an RLDE405-12-6 CW laser @405 nm and collecting the sample emission with an SM442 spectrometer.

RESULTS & DISCUSSION

Photoluminescence Quantum Yield

All the samples show PLQY above 30%. The lowest values are found for DDAB and OAcOAm samples, with 32% and 36%, respectively.

The lecithin capped NCs film show a PLQY of 54%, while a remarkable value of 84% is found in the ASC18 sample.

Amplified Spontaneous Emission

All the films show ASE under nanosecond pumping, evidenced by the appearance of a narrow emission band as the excitation density is increased (see Figure on the right, showing the excitation density dependence of the emission spectra of the lecithin sample).

The typical threshold is on the scale of few mJcm⁻², while the lecithin sample show a threshold of only 0.36 mJcm⁻², which is one of the lowest values ever reported under nanosecond pumping.

Environmental sensitivity

We investigated the emission spectra dependence on the sample environment (vacuum vs air).

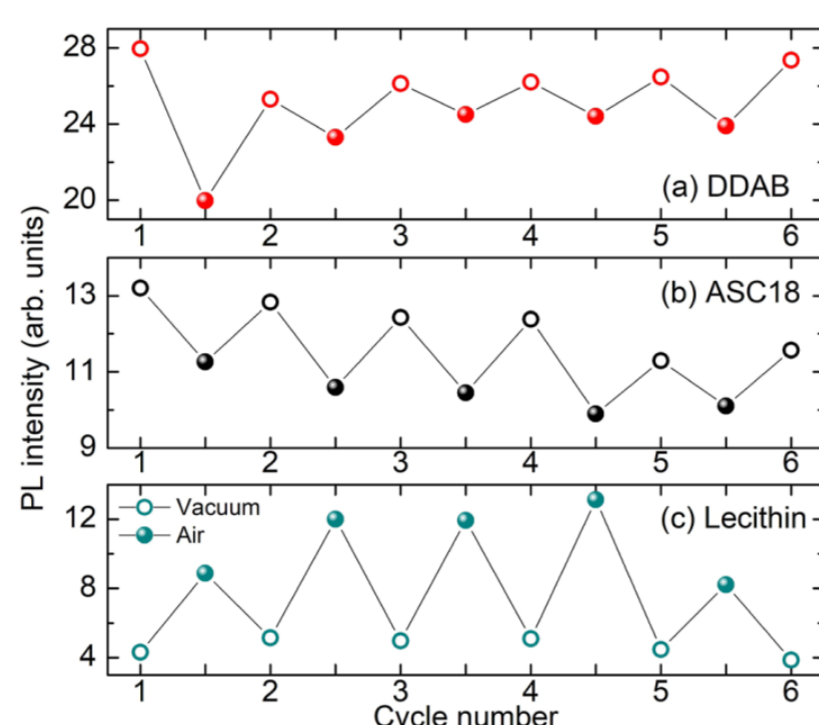
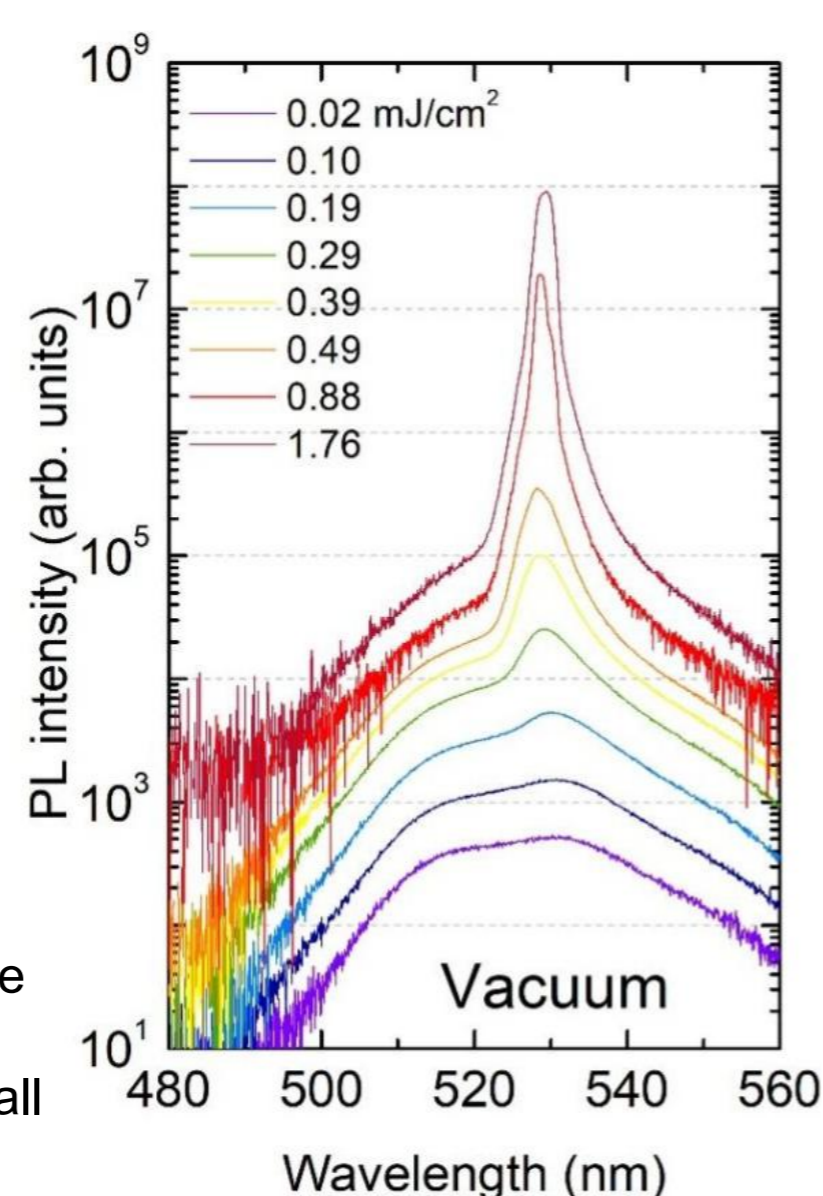
No effects are observed on the OAcOAm sample, while all the other films show a reversible intensity modulation when the environment is changed.

The intensity modulation is always higher for ASE than for spontaneous emission.

A reversible quenching of about 20% is observed for ASE of ASC18 and DDAB sample, ascribed to moisture induced surface solvation, resulting in a less effective passivation in air.

On the contrary lecithin sample show an initial modulation with lower intensity in air, followed by a switch after few air-vacuum cycles, with lower emission in air, suggesting the irreversible formation of surface defects after few cycles, that are reversibly passivated by oxygen and moisture.

This effects could be exploited for the realization of optical gas sensors based on perovskite NCs showing ASE.



Sample comparison

	OAcOAm	DDAB	ASC18	Lecithin
PLQY	36%	32%	84%	54%
ASE threshold	2.7 mJ/cm ²	1.7 mJ/cm ²	3.2 mJ/cm ²	0.36 mJ/cm ²
Sensitivity	0%	20%	20%	60%

A visual comparison of the ligand effect on the investigated properties is reported above, where we assigned a color level to each tab, from worst (red tab) to best (green tab).

The OAcOAm film shows a very high ASE threshold, and the presence of air does not influence its optical response; in addition it shows a relatively low PLQY.

The DDAB sample show a lower ASE threshold and a moderate sensing activity with a 20% RQ response in the presence of air, but the lowest PLQY.

Similar ASE sensitivity was observed with the ASC18-capped NC thin film, showing the best PLQY, but also the highest ASE threshold.

Finally, the lecithin-capped NC film is the only one that combines a high PLQY with excellent ASE properties and high ambient air sensitivity. It indeed shows the lowest ASE threshold the highest sensitivity to ambient air.

CONCLUSION

We demonstrated that the choice of the ligand strongly affects the spontaneous emission and the ASE properties, and the NCs emission intensity modulation due to the environment variation.

Our results suggest that the optimization of specific properties can be obtained by a proper choice of the ligand.

REFERENCES

Stefania Milanese, Maria Luisa De Giorgi,* Giovanni Morello, Maryna I. Bodnarchuk, and Marco Anni [ACS Appl. Nano Mater. 2025, 8, 3964-3973](#)