A-SITE CATION ENGINEERING IN A TWO-DIMENSIONAL RUDDLESDEN-POPPER PEROVSKITE

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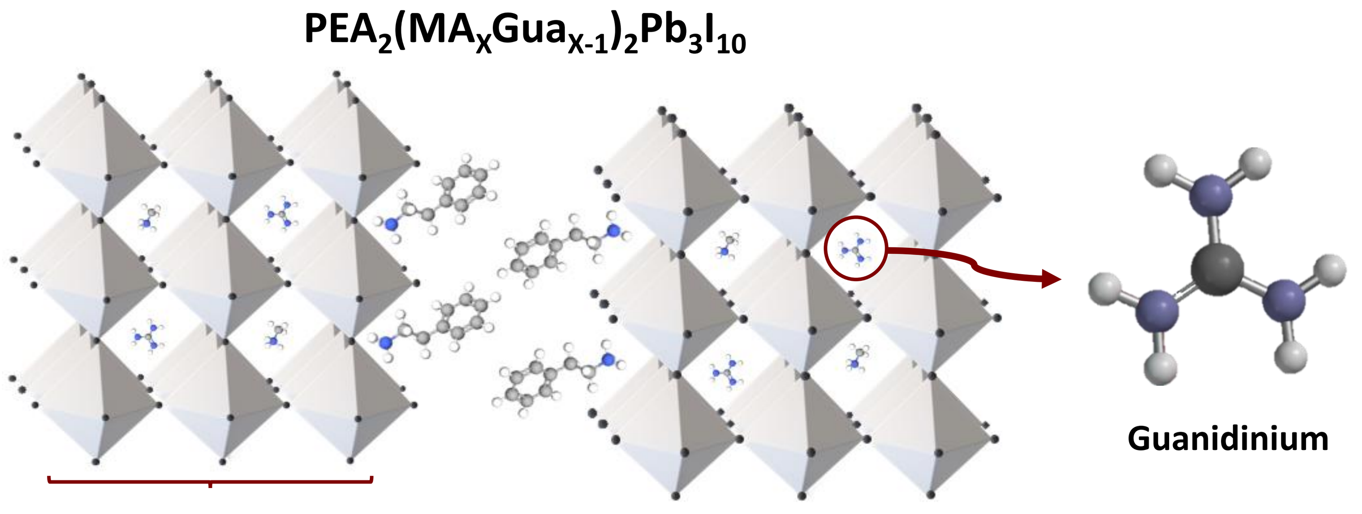
Abstract

Currently, organic-inorganic hybrid perovskites (PHOI) with three-dimensional (3D) crystalline structure are widely used in optoelectronic devices (e.g. solar cells). However, due to the environmental degradation suffered by the 3D perovskites, the two-dimensional (2D) PHOIs have risen as an alternative since the incorporating of larger organic cations between the "perovskite slabs" mitigates the degradation. The 2D perovskites, in particular the Ruddlesden-Popper (RP) phases, show ample flexibility regarding the organic cations that can be incorporated between the "perovskite slabs". However, the small organic cations inserted in the octahedral voids have so far been limited to those that meet the Goldschmidt tolerance factor ($0.8 \le t \le 1$). In this work, the incorporation of a bulky organic cation (guanidinium, Gua) that exceeds the tolerance factor (t = 1.03) has been studied for the first time. The methylammonium cation (MA) has been gradually replaced by the Gua cation in the $PEA_2MA_{n-1}Pb_nI_{3n+1}$ (PEA, phenylethylammonium) perovskite with n = 3 to synthesize thin films. The sequential insertion of Gua into the network up to 90% and its key role in controlling the distribution of n members is demonstrated. Finally, a significant improvement in the stability of the films is tested against environmental factors even at low percentages of Gua.

Introduction

$PEA_2(MA_XGua_{X-1})_2Pb_3I_{10}$



Goldschmidt tolerance factor

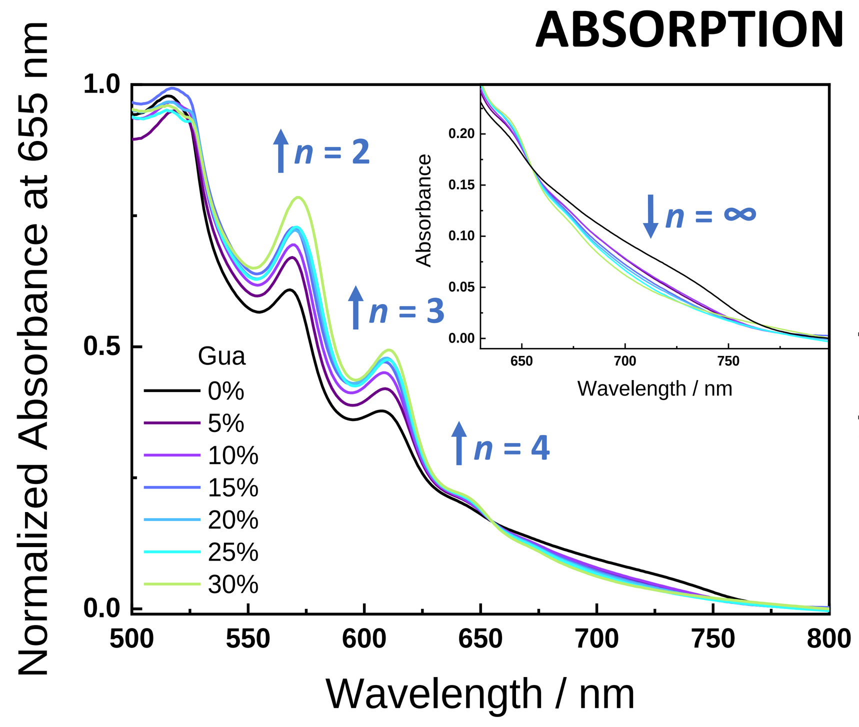
$$t = \frac{r_A + r_X}{\sqrt{2(r_B + r_X)}}$$

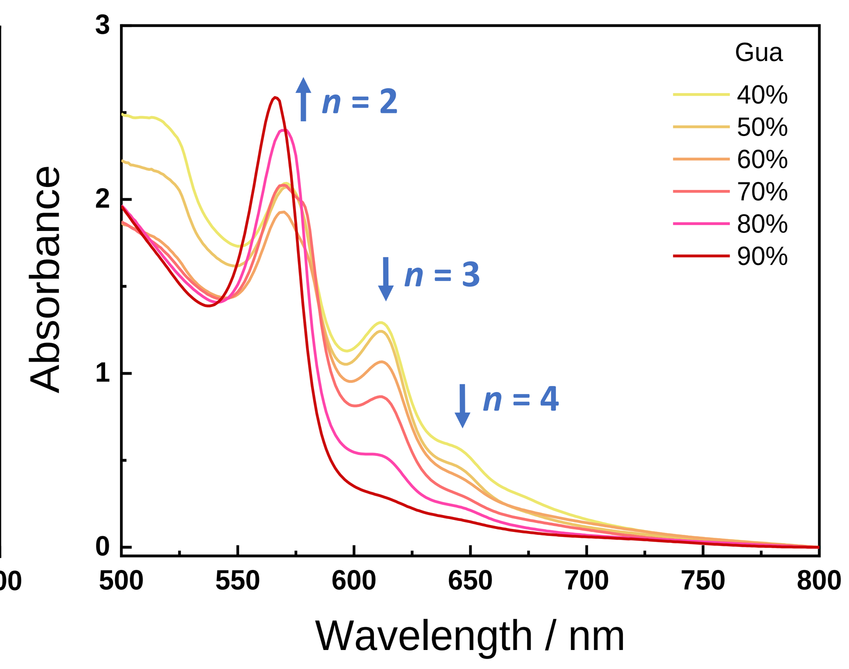
$0.8 \le t \le 1$

t_{Gua} = 1.03

Optical characterization

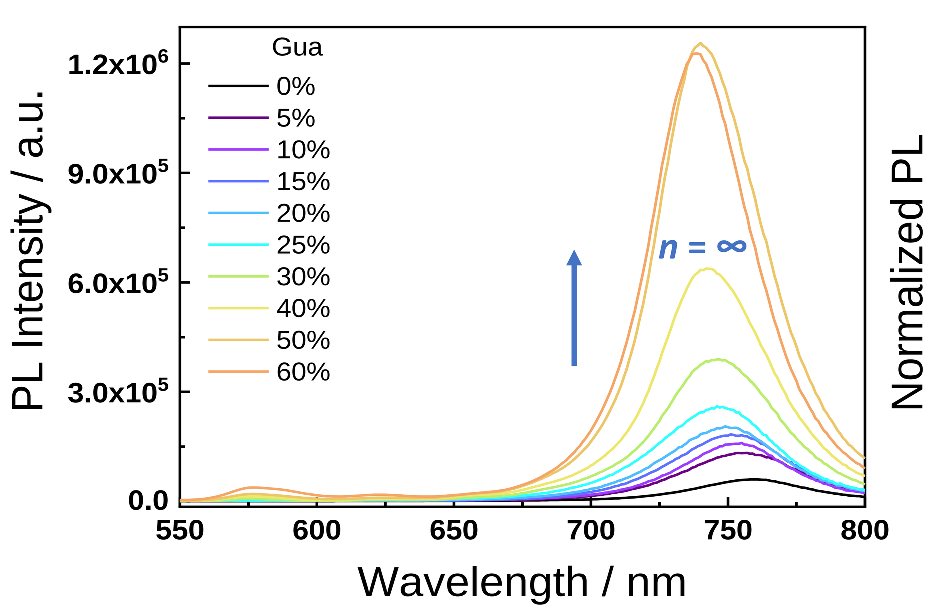
ABSORPTION SPECTROSCOPY

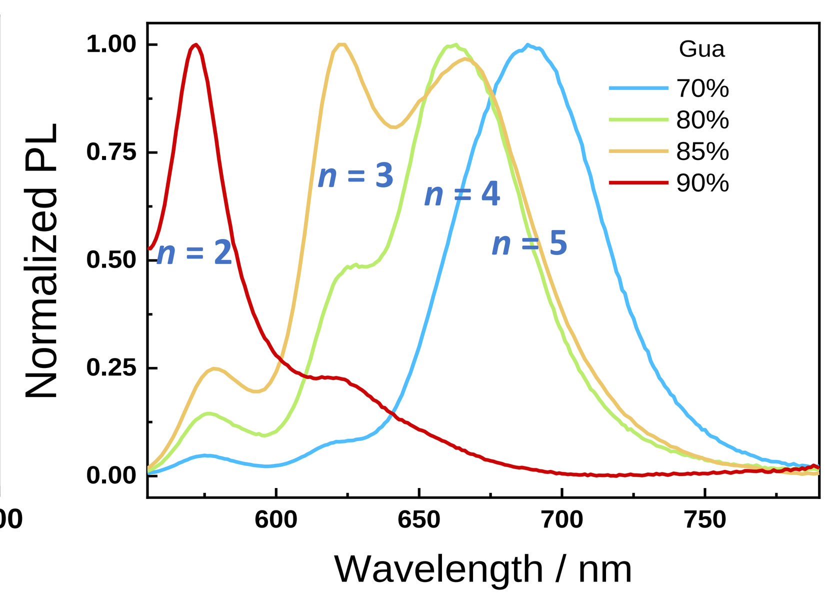




↑ Gua ⇨ n < 5 **↑ Gua ⇨ n = 2**

PHOTOLUMINESCENCE MEASUREMENTS

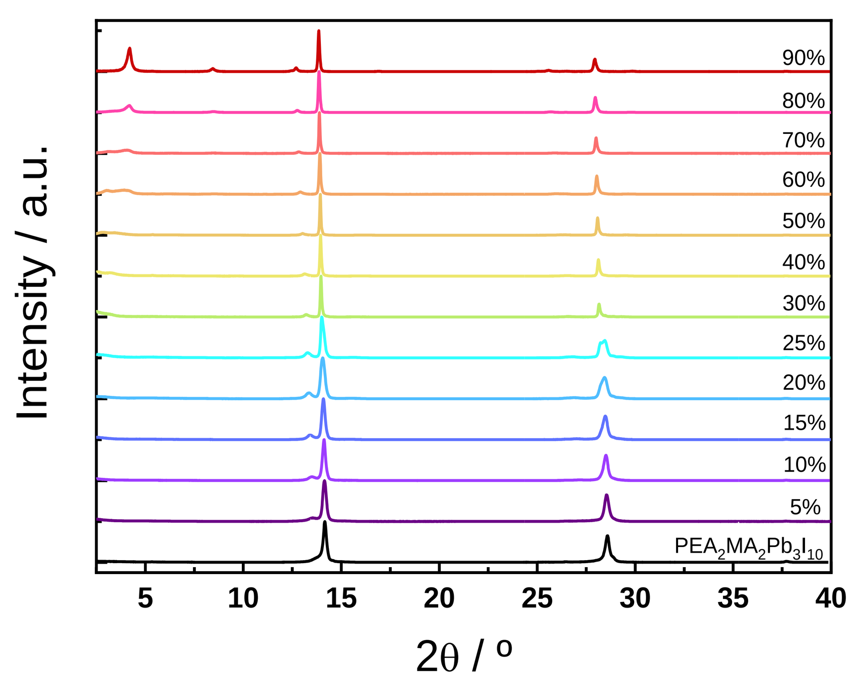


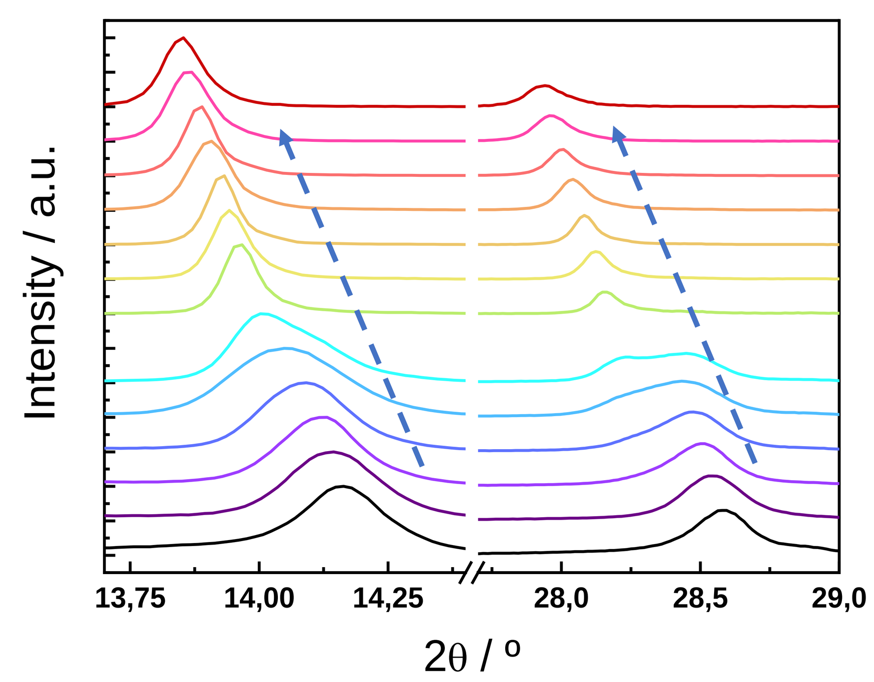


Increase of the PL **Precise control of n**

Structural characterization

X-RAY DIFFRACTION

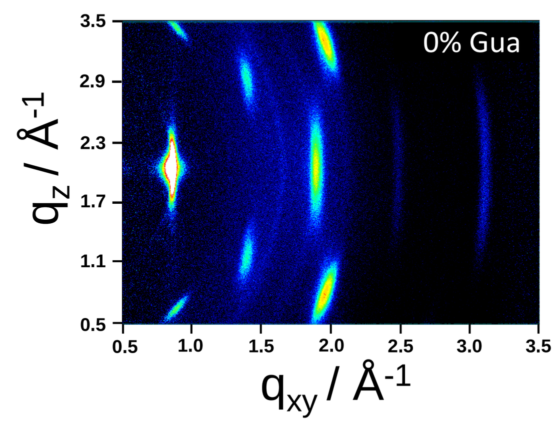


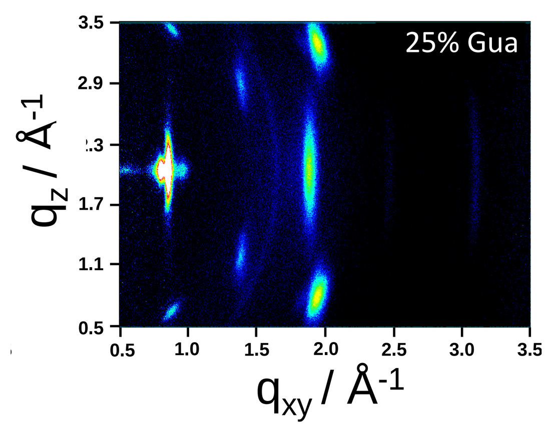


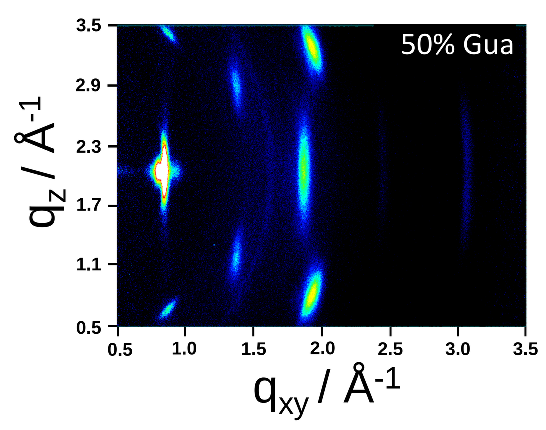
No new reflection peaks ⇩ No new crystallographic phases

Regular expansion of the unit cells ⇩ Sequential incorporation of Gua

GIWAXS

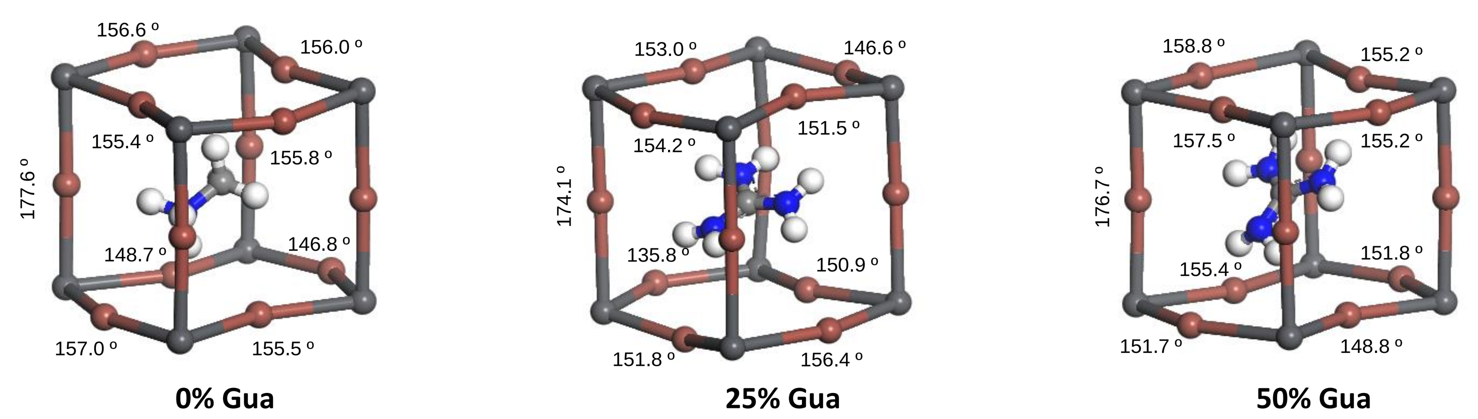






Preservation of preferential orientation

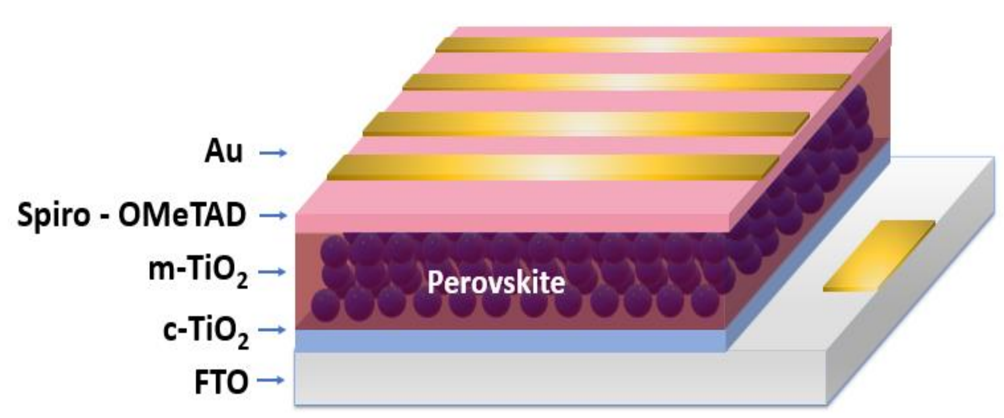
DFT-GGA CALCULATION



Small distortions ⇨ No impact on structure stability

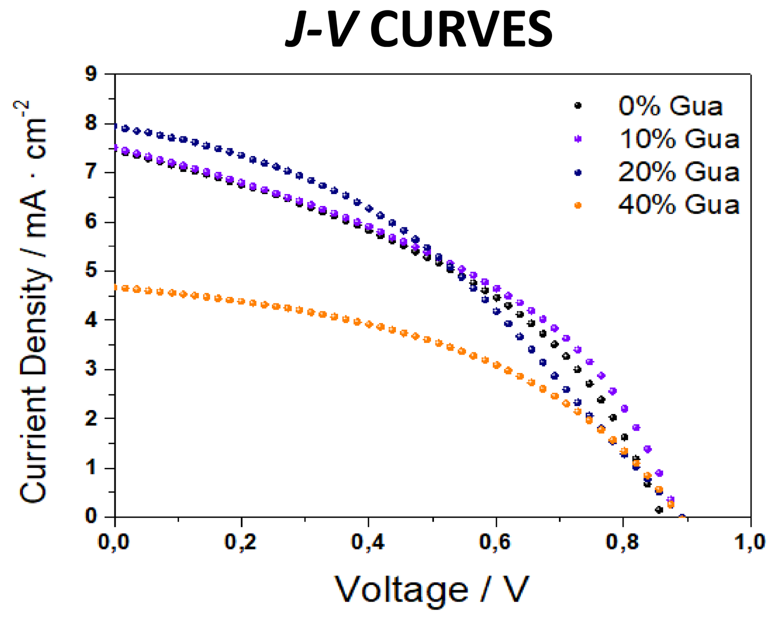
Photovoltaic parameters and device stability

DEVICE ARCHITECTURE

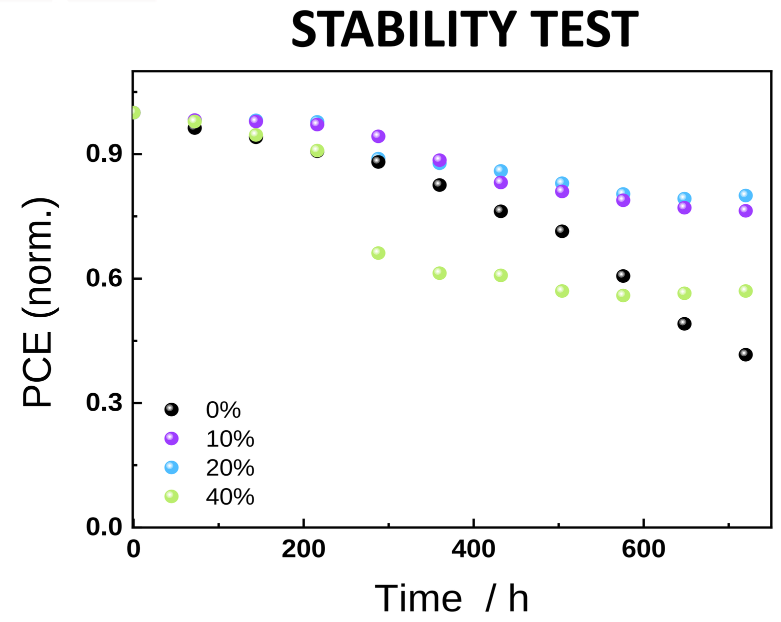


J-V CURVES

PCE ≈ 2.7 % up to 20% Gua



STABILITY TEST



Gua slows down the perovskite degradation

Devices conserved in dark under constant fixed relative humidity (RH) and temperature conditions (~50% RH and 25 ºC) without encapsulation

Conclusions

- The Gua is incorporated into the octahedral voids of the "perovskite slabs" of the perovskites RP up to 90% without loss of preferential orientation.
- The insertion of Gua occurs preferably in the phases of low dimensionality (n <5).
- The incorporation of the Gua leads to a significant improvement in the stability of the films against environmental factors.

References and acknowledgment

1. Cao, D. H. et al. 2D Homologous Perovskites as Light-Absorbing Materials for Solar Cell Applications. *J. Am. Chem. Soc.* **2015**, *137* (24), 7843–7850.
2. **Ramos-Terrón, S. et al. Relaxing the Goldschmidt Tolerance Factor: Sizable Incorporation of the Guanidinium Cation into a Two-Dimensional Ruddlesden–Popper Perovskite. *Chem. Mater.* 2020, 32, 9, 4024-4037**

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