Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

The role of organic cations as additives in photovoltaic perovskites.

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Table 1 shows the relationship between adsorption energy and power conversion efficiency (PCE) reported by Wang et al. [1]

Table 1: Relationship of adsorption energy and PCE.

Additive	PCE(%)	E_{ads}(eV)
Theophylline	23.48	-1.70
Caffeine	22.32	-1.30
Theobromine	20.24	-1.10

Structural configurations

To choose the model, we perform an analysis of the surface energy per layer, this is shown in the Fig. 1 and the following equation is evaluated:

$$\sigma = \frac{E_{slab} - n * E_{bulk}}{A} \tag{1}$$

where E_{slab} is the total energy of the slab material (eV), E_{bulk} is the total energy of the bulk material (eV), n is the number of atoms involved in the slab, and A is the surface area ($\mathring{A}^2$). Here, the energy is observed to converge when the number of layers is increased, however, there is no significant change in the energy value. Furthermore, we use on purpose the same number of layers as in reference [1] to be able to accurately compare our results with a theoretical-experimental study. The two layers were fixed at the bottom of the surface model to simulate a semi-infinite bulk perovskite.

The four initial horizontal configurations are shown in Fig.2 explicitly.

The six minimum energy configurations after relaxation of the perovskite/additive systems are shown in Fig.3. It shows clearly how the carbonyl oxygen occupy the vacant sites of I. This is the place where the formation of the octahedrons occurs.

Energy adsorption

The following table lists the adsorption energy values obtained for the 30 configurations studied. The analysis presented in this work, is only based in the minimum energy configurations.

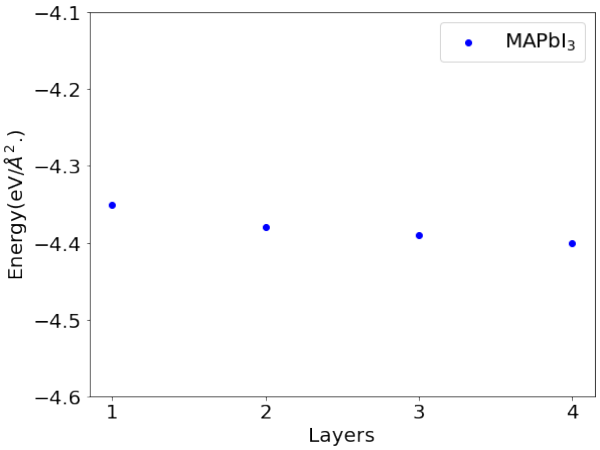
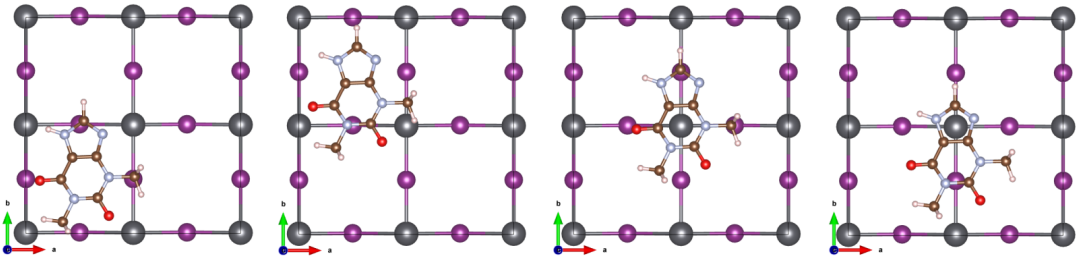


Figure 1: Horizontal configurations sites.



(a) Configuration H_1 **(b)** Configuration H_2 **(c)** Configuration H_3 **(d)** Configuration H_4

Figure 2: Horizontal configurations sites.

Table 2: Adsorption energies of organic molecules and organic cations on the cubic [001]-PbI_2 surface.

Additive	E_{ads}**(eV)**	**Additive**	E_{ads}**(eV)**	**Additive**	E_{ads}**(eV)**
Theophylline H_1	-1.97	Theobromine H_1	-1.98	Caffeine H_1	-2.05
Theophylline H_2	-2.63	Theobromine H_2	-2.03	Caffeine H_2	-1.84
Theophylline H_3	-2.56	Theobromine H_3	-1.58	Caffeine H_3	-1.73
Theophylline H_4	-2.45	Theobromine H_4	-2.12	Caffeine H_4	-2.10
Theophylline V	-2.04	Theobromine V	-1.19	Caffeine V	-0.90
Theophylline$^+$ H_1	-3.24	Theobromine$^+$ H_1	-2.85	Caffeine$^+$ H_1	-3.26
Theophylline$^+$ H_2	-3.08	Theobromine$^+$ H_2	-3.01	Caffeine$^+$ H_2	-3.02
Theophylline$^+$ H_3	-3.15	Theobromine$^+$ H_3	-2.83	Caffeine$^+$ H_3	-2.75
Theophylline$^+$ H_4	-3.20	Theobromine$^+$ H_4	-3.26	Caffeine$^+$ H_4	-3.34
Theophylline$^+$ V	-2.28	Theobromine$^+$ V	-2.24	Caffeine$^+$ V	-2.36

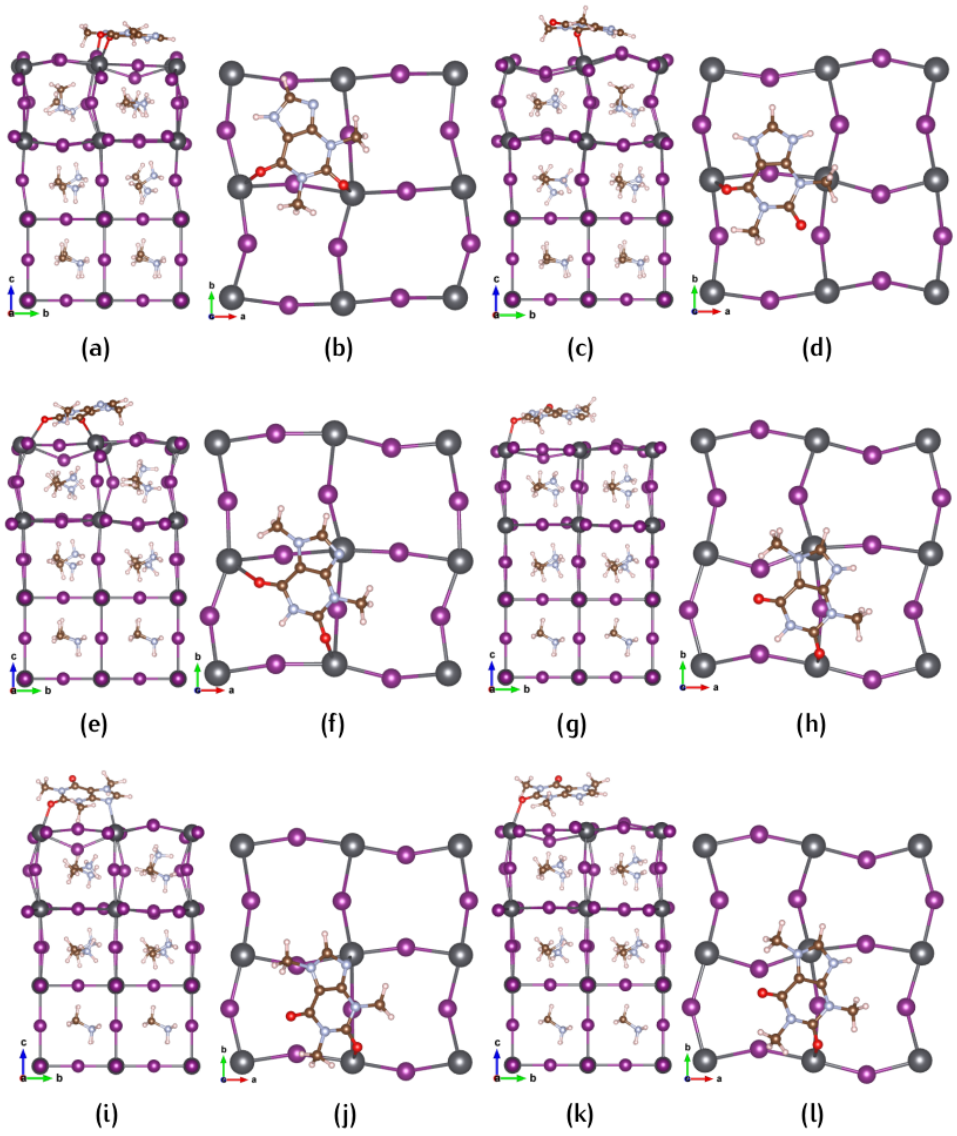


Figure 3: Lower adsorption energy configurations. (a) Theophylline, (c) theophyline^{+}, (e) theobromine, (g) theobromine^{+}, (i) caffeine, (k) caffeine^{+} and (b),(d),(f),(h),(j)(l) are top views.

The formulas for evaluating the adsorption energy by contribution are described below. The adsorption energy corresponding to the Van der Waals energy is calculated as:

$$E_{vdW} = (E_{sys-with-vdW} - E_{sys-without-vdW}) - (E_{surf-with-vdW} - E_{surf-without-vdW}) - (E_{additive-with-vdW} - E_{additive-without-vdW}) \quad (2)$$

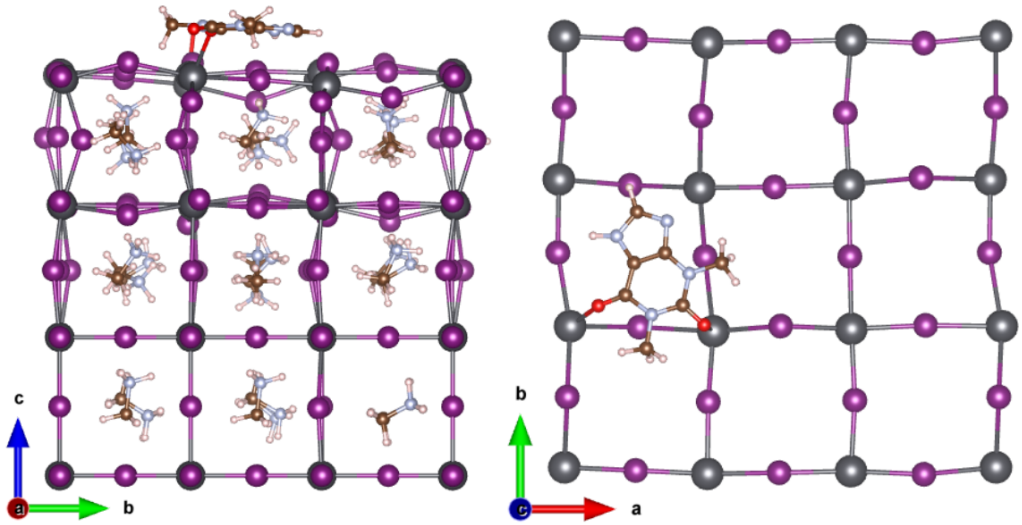
To evaluate the effect of atomic surface relaxation, the additives are canceled and the formula is as follows:

$$\begin{aligned} E_{relax} &= E_{ads/surf-relax} - E_{ads} \\ &= E_{surf-relax} - E_{surf} \end{aligned} \quad (3)$$

Finally, the interaction energy of the additive with the surface is calculated as:

$$E_{int} = E_{ads} - E_{vdW} - E_{relax} \quad (4)$$

To determine the effect of surface size, we perform a calculation for a larger surface with the most reactive molecule. Fig.4 shows this system, the cell has been increased by $2^{0.5}$a×$2^{0.5}$a×1. Here it is observed that the formation of the two octahedrons of the carbonyls with the Pb on the surface is present too as with the smaller surface.



(a) (b)

Figure 4: Theophylline. (a)Lateral view and (b)top view.

Table 3 shows a comparative values of the adsorption energies for the 2x2 and 3x3 supercells for the most reactive molecular additive (theophylline). In the 3x3 model, the contribution to the van der Waals energy increases due to the size of the system, however, the comparison of the adsorption energies without the van der Waals contribution gives the same value in both systems. Although the ideal would be to use a larger surface model, we think that good approximations are obtained with our model. We have sought a balance between computational cost and accuracy.

Table 3: Comparative values of the adsorption energies for the 2x2 and 3x3 supercells.

Supercell model	E_{ads} (eV)	E_{vdW} (eV)	E_{ads}-E_{vdW} (eV)
2x2	-2.63	-1.02	-1.61
3x3	-2.71	-1.11	-1.61

Charge Transfer

Table 4 shows the charge transfer for the additives of minimum adsorption energy.

Table 4: Charge transfer for additives with minimum energy of adsorption.

Additive	Max Δ Q (electron transfer e)
Theophylline H_2	0.136
Theophylline$^+$ H_1	0.258
Theobromine H_4	0.083
Theobromine$^+$ H_4	0.267
Caffeine H_4	0.132
Caffeine$^+$ H_4	0.267

References

[1] R. Wang, J. Xue, K.-L. Wang, Z.-K. Wang, Y. Luo, D. Fenning, G. Xu, S. Nuryyeva, T. Huang, Y. Zhao, J. Yang, J. Zhu, M. Wang, S. Tan, I. Yavuz, K. Houk, and Y. Yang, "Constructive molecular configurations for surface-defect passivation of perovskite photovoltaics," *Science (New York, N.Y.)*, vol. 366, pp. 1509–1513, 12 2019.