

## Article

# Improved Perovskite Structural Stability by Halogen Bond from Excessive Lead Iodide via Numerical Simulation

Taoran Wang <sup>1,\*</sup>, Fan Xu <sup>2</sup> , Qi Wang <sup>3</sup>, Lu Tai <sup>3</sup> and Gu Xu <sup>3</sup>

<sup>1</sup> Energy Materials and Optoelectronics Unit, Songshan Lake Materials Laboratory, China Academy of Sciences, Dongguan 523808, China

<sup>2</sup> State Key Laboratory for Artificial Microstructure and Mesoscopic Physics, School of Physics, Frontiers Science Center for Nano-optoelectronics, Collaborative Innovation Center of Quantum Matter, Peking University, Beijing 100871, China; xufan@pku.edu.cn

<sup>3</sup> Department of Materials Science and Engineering, McMaster University, 1280 Main St. W, Hamilton, ON L8S 4L8, Canada; wangq166@mcmaster.ca (Q.W.); tai4@mcmaster.ca (L.T.); xugu@mcmaster.ca (G.X.)

\* Correspondence: wangtaoran@sslabor.org.cn

**Abstract:** The short lifetime of perovskite solar cell devices limits the application of the technique, which is yet to be resolved, despite many attempts. An important step is made here by the numerical modelling method, which reveals the decomposition kinetics under the protection of halogen bonds from excess  $\text{PbI}_2$ . Irregular diffusion behaviour of water molecules is observed when excessive  $\text{PbI}_2$  is introduced, possibly due to the passivation and hindrance from the halogen bond, resulting in a lifetime enhancement of at least five times. The detailed kinetics are also obtained by analyzing the decomposition rate curve, offering a possible path towards high-stability PCE perovskite solar devices, by increasing the  $\text{PbI}_2$  concentration to above the threshold, which opens an unprecedented route in perovskite solar cell research, and is, hopefully, of intrinsic interest to the broad materials research community as well.

**Keywords:** improved perovskite stability; irregular diffusion; halogen bond modelling



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## 1. Introduction

Organic–inorganic perovskite materials attracted much attention in the past decade, due to their low manufacturing costs and high light-absorbing properties [1,2]. Such a structure demonstrated the advantages of a tunable bandgap, high absorption coefficient, long exciton diffusion length, high carrier mobility, and low exciton binding energy, which rapidly boosted the power conversion efficiency (PCE) [3–5]. The devices based on  $\text{FAPbI}_3$  show a record-breaking PCE of 25.7%, making them completely comparable to the commercially available Si panels [6]. Nevertheless, the commercialization of such devices was hindered greatly by their instability, leading to a limited lifetime, which only reached 10,000 h under even the best encapsulation [7–9], still far away from the 20 years lifetime of an Si panel [10,11]. The instability is caused by substances in the air, such as moisture and oxygen [12–14]. In addition, the diffusion of those substances in the perovskite film can be accelerated by the imperfections in the film [15], such as defects or grain boundary areas, resulting in a much lower lifetime [16–18]. The influence of the imperfections is aggravated in the industrial fabrication environment, making them a serious obstacle for application [19,20].

To overcome this challenge, researchers adopted many strategies to improve the film quality [21–23]. Advanced film deposition methods, including blade coating, slot-die coating, inkjet printing, and chemical vapor deposition [24–27], were investigated to reduce the imperfections and to produce a large area perovskite device. Despite the slightly improved device performance, those methods have yet to solve this problem

completely [28–30]. More importantly, some of their results are not reproducible, which is even more serious for industrial application [19]. A breakthrough was achieved recently, when researchers improved the device stability by adding excess  $\text{PbI}_2$  during the perovskite-synthesizing step [31–34]. It is found that excess lead iodide not only precipitates at the grain boundary, passivating the imperfection area [35,36], but also forms halogen bonds with the neighboring organic cations [37,38], enhancing the structural stability. In addition, the PCE performance of perovskite solar cells could also be enhanced by the excess  $\text{PbI}_2$ , possibly due to the shorter charge carrier extraction time [39]. Unfortunately, such devices eventually decomposed in the air, possibly due to the lack of understanding of the kinetic details of perovskite decomposition, vis-à-vis the moisture diffusion inside the perovskite film, under the influence of a halogen bond [40,41].

It is, therefore, the purpose of this research to explore the kinetics of moisture diffusion inside the perovskite film under the effect of a halogen bond. Due to the difficulty of observing the alteration of the halogen bond in the perovskite structure, it is necessary to construct a numerical model to simulate the moisture diffusion, the breakdown of the halogen bond, and the associated decomposition of perovskite film. The simulation was started by introducing some water molecules at the edge of the film, which diffused along the imperfections and led to the cascade decomposition of the perovskite structure. The simulated results demonstrate the increased grain boundary area caused by the excess  $\text{PbI}_2$ , which is passivated by the precipitated  $\text{PbI}_2$  during the annealing process, forming a large amount of halogen bonds. Such a bond is beneficial for the stability, as it hinders the water molecule diffusion, leading to non-Fickian behaviour, especially at 15% excess  $\text{PbI}_2$ . These results fill in the missing part of the moisture diffusion under hindrance, providing not only scientific support for more stable and efficient PSC devices, but also bringing fresh kinetic inspiration, enabling us to control the diffusion process by chemical bonding.

## 2. Modelling

A 2-dimensional lattice of  $100 \times 100$  sites was constructed by Python, as was adopted previously [42]. The size of the lattice was conveniently chosen as the previous experimental work shows similar results on various sample sizes. Each site represents the smallest repeating unit of the perovskite single crystals, which opens a path for water diffusion when collapsed.  $\text{MAPbI}_3/\text{FAPbI}_3$  was chosen to represent the most common organic perovskite structure; any other organic perovskite structure could also be adopted, which will not alter the modelling results due to the sensitivity to the moisture. To accommodate the irregular diffusion, which is accelerated by the collapsed site, as was reported previously, it was built into the simulation water level variables  $W$ , and updated in each iteration. The decomposition probability variable in each site was connected to the water level of its neighboring diffusion path, including left, right, up, and down, represented by  $W(x,y,d = 1-4)$ , and the value was updated during the simulation process. The  $P$  value of a site can be calculated by the master equation that incorporates both  $P$  and  $W$  values of its four neighboring sites, as shown in Equation (1).

$$\frac{dP_i}{dt} = \sum_j (P_j W_{ji} - P_i W_{ij}) \quad (1)$$

The formula shows the relationship between these values and their contribution to the newly updated  $p$ -value at that point. The number of water paths increases over time, as the perovskite site is constantly collapsing. For example, the  $W(x,y,d)$  value can be randomly assigned between 0 and 0.6 in the beginning to allow the diffusion to occur, which represents the imperfections in the perovskite film. To simulate the influence of the halogen bond from the excess  $\text{PbI}_2$ , a fresh variable HB needs to be introduced to each site, indicating the strength of the halogen bond there. The initial value is randomly distributed throughout the whole lattice, based on the amount of excess  $\text{PbI}_2$  adopted, simulating the

influence of  $\text{PbI}_2$  concentration on the grain boundary area. The value of HB is randomly chosen between 0 and 0.07 eV, as was reported in the literature.

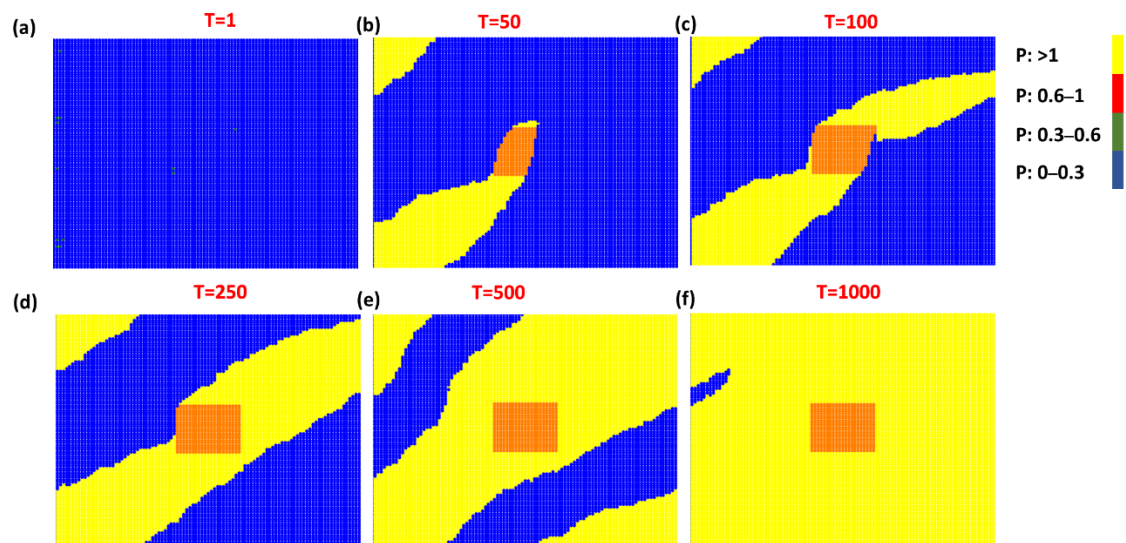
Next, the value of  $W(x,y,d)$  was updated in each iteration. When the  $P(x,y)$  value reached 0.3, its  $W(\text{right})$  or  $W(\text{left})$  value was altered to 1.0 by 50/50 chance, meaning the partial decomposition of the perovskite structure. When the  $P(x,y)$  value reached 0.6, both  $W(\text{right})$  and  $W(\text{left})$  values were altered to 1.0, leaving only the  $W(\text{top})$  and  $W(\text{down})$  values unchanged, which formed vertically oriented one-dimensional  $\text{PbI}_2$  chains, simulating collapsed perovskites. In order to demonstrate the possible directional effects, a boxed area was selected near the center of the lattice, where the previously mentioned  $W(\text{right})/W(\text{left})$  values were switched to  $W(\text{up})/W(\text{down})$ , e.g., 1D  $\text{PbI}_2$  chains in horizontal orientation within the boxed area. The HB value, on the other hand, does not need to be altered after each iteration, simply because when water diffuses to a site and decomposes the perovskite, its HB value no longer affects the decomposition of the remaining perovskite, as observed in experiments.

### 3. Results and Discussion

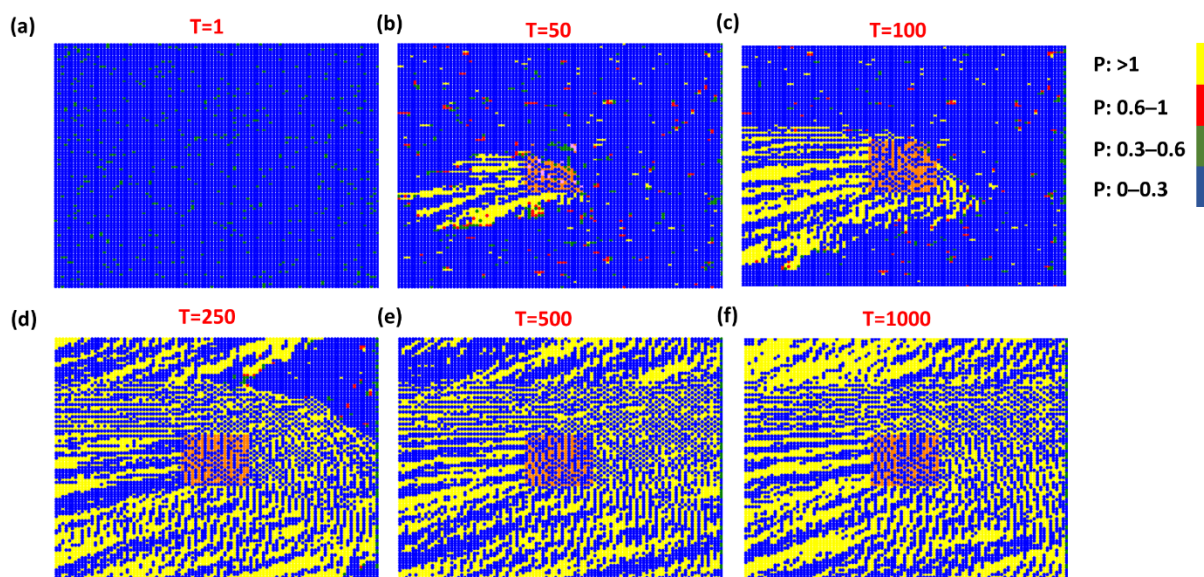
Based on the discovery of the enhancement of the PSC performance by excess  $\text{PbI}_2$ , the influence of a halogen bond on the organic perovskite to withstand the moisture attack was numerically simulated by 2D lattice, and some surprising results were observed, originating from the fact that the diffusion paths were constantly changing as influenced by halogen bonds.

To simulate the cascade degradation triggered by water molecules in reality, decomposition was randomly induced at some sites on the left side of the lattice, so that the water could start to diffuse, instead of setting the  $P$  value on the left side to 1. The results are best demonstrated by the time evolution picture of the water diffusion, as depicted by a snapshot of the entire lattice in Figure 1, during which the molar ratio of  $\text{PbI}_2$  and organic halide is set to 1:1. The  $P$  value of the whole lattice is relatively low at the beginning, representing only a few green sites ( $p > 0.3$ ), meaning less defects in this case. Despite the good quality of the perovskite film, the water diffuses rapidly in the lattice, as shown in Figure 1b–f. The number of blue sites indicates the remaining perovskite, which is recorded as 8271 for iteration number ( $T$ ) = 50, 7598 for  $T$  = 100, 5455 for  $T$  = 250, 2742 for  $T$  = 500, and 185 for  $T$  = 1000. As curve-fitted in the following figure, which demonstrates exponential decay, indicating that the diffusion rate is enhanced by the decomposed site.

The exponential decay also provides a kinetic implication, as diffusion needs to overcome the energy barrier, and the proportion of molecules that meet the criteria can be given by  $\exp(-E_a/RT)$ , where  $E_a$  represents the activation energy for water diffusion. Such energy can be offset by the structural defects, which provide more free space for water molecules to diffuse. The activation energy could, thus, be obtained from the fitted curve, providing a kinetical understanding of the degradation. In the next modelling, excess  $\text{PbI}_2$  was induced, which alters the water diffusion process, as shown in Figure 2, during which the molar ratio of  $\text{PbI}_2$  and organic halide is set to 1.05:1. In Figure 2a, more green sites are observed, indicating the increased grain boundary area due to the excess  $\text{PbI}_2$ . Although the imperfection area is enlarged, it can be passivated by  $\text{PbI}_2$  via an in situ mechanism, as reported previously [43,44], which hinders the water diffusion by the halogen bond, as demonstrated in Figure 2b–f, where irregular diffusion is observed. In Figure 2b,c, the water first diffuses inward from the weak point on the left, and next the backward diffusion from right to left side is observed, meaning the halogen bond on the left side is broken. The number of blue sites is recorded as 9855 for iteration number ( $T$ ) = 1, 8881 for  $T$  = 50, 8138 for  $T$  = 100, 5380 for  $T$  = 250, 5090 for  $T$  = 500, and 4679 for  $T$  = 1000. The curve-fitted line indicates that the decomposition exhibits an exponential trend, with some deviated points, proving that the activation energy for water diffusion is enhanced by the halogen bond, resulting in an extended lifetime for the perovskite.



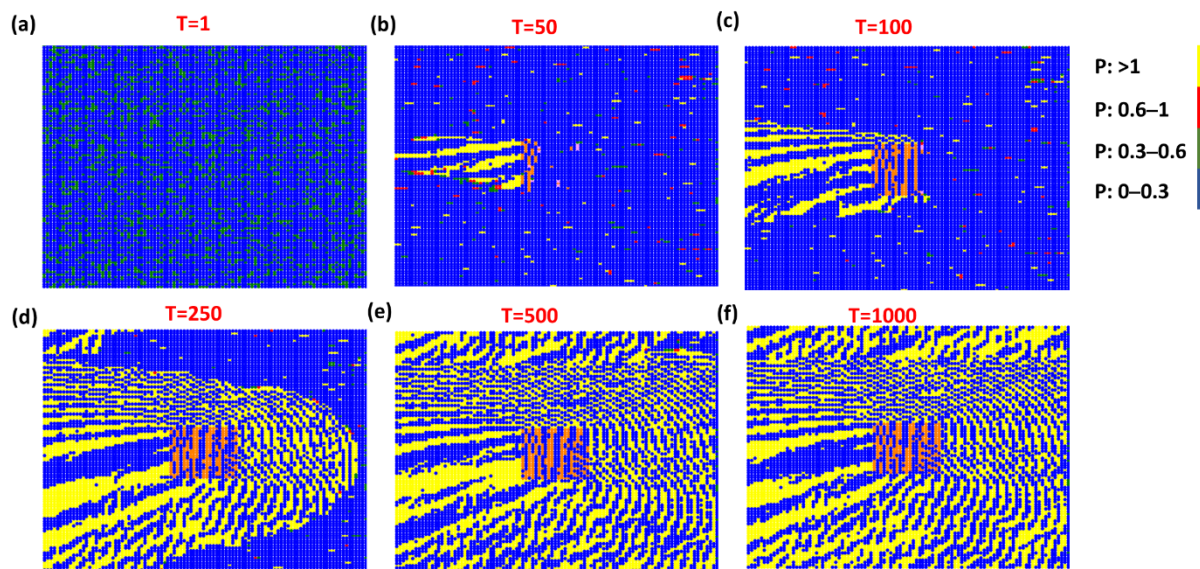
**Figure 1.** (a) The simulation results of 1 iteration when no excess  $\text{PbI}_2$  is introduced. Blue =  $P: 0-0.3$ ; green =  $P: 0.3-0.6$ ; red =  $P: 0.6-1$ ; and yellow (orange) (within the central box) =  $P \geq 1.0$ , iteration number represents the diffusion time. (b) The simulation results of 50 iterations when no excess  $\text{PbI}_2$  is introduced. (c) The simulation results of 100 iterations when no excess  $\text{PbI}_2$  is introduced. (d) The simulation results of 250 iterations when no excess  $\text{PbI}_2$  is introduced. (e) The simulation results of 500 iterations when no excess  $\text{PbI}_2$  is introduced. (f) The simulation results of 1000 iterations when no excess  $\text{PbI}_2$  is introduced.



**Figure 2.** (a) The simulation results of 1 iteration when 5% excess  $\text{PbI}_2$  is introduced. Blue =  $P: 0-0.3$ ; green =  $P: 0.3-0.6$ ; red =  $P: 0.6-1$ ; and yellow (orange) (within the central box) =  $P \geq 1.0$ , iteration number represents the diffusion time. (b) The simulation results of 50 iterations when 5% excess  $\text{PbI}_2$  is introduced. (c) The simulation results of 100 iterations when 5% excess  $\text{PbI}_2$  is introduced. (d) The simulation results of 250 iterations when 5% excess  $\text{PbI}_2$  is introduced. (e) The simulation results of 500 iterations when 5% excess  $\text{PbI}_2$  is introduced. (f) The simulation results of 1000 iterations when 5% excess  $\text{PbI}_2$  is introduced. Non-Fickian diffusion is observed.

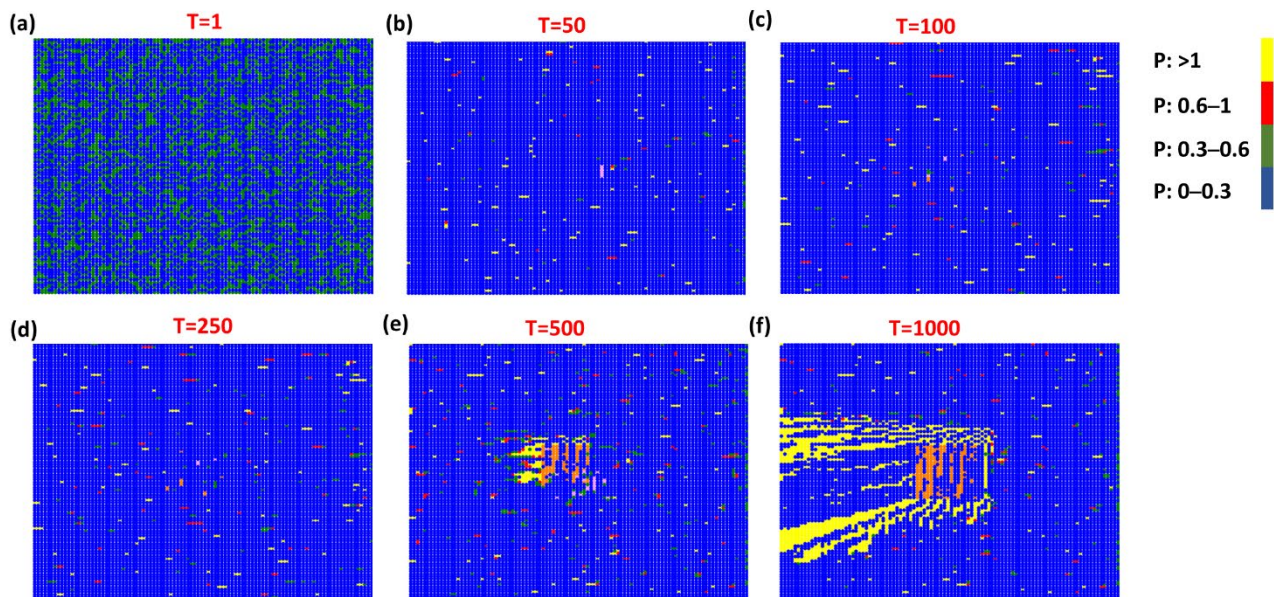
The grain boundary is further increased when the molar ratio of  $\text{PbI}_2$  and organic halide is set to 1.1:1, as shown in Figure 3. In Figure 3a–f, the number of blue sites is recorded as 9864 for iteration number ( $T$ ) = 1, 9275 for  $T$  = 50, 8869 for  $T$  = 100, 6319 for  $T$  = 250, 5295 for  $T$  = 500, and 4863 for  $T$  = 1000. It is apparent that the water becomes more

difficult, due to the raised number of halogen bonds, which is especially obvious in the early stages, as indicated in Figures 3–5, where the points deviate more in the early stages. This proves that the presence of the halogen bond impedes the water diffusion at the beginning of the decomposition, which is important for the maintenance of stability. However, as time evolves, the degradation rate returns to an exponential trend, due, probably, to the breakdown of the halogen bond in this stage.

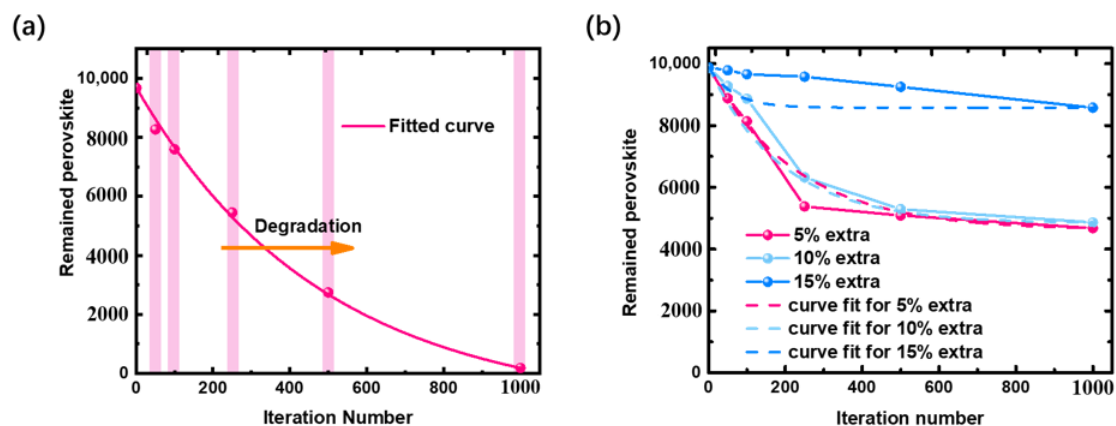


**Figure 3.** (a) The simulation results of 1 iteration when 10% excess  $\text{PbI}_2$  is introduced. Blue =  $P: 0-0.3$ ; green =  $P: 0.3-0.6$ ; red =  $P: 0.6-1$ ; and yellow (orange) (within the central box) =  $P \geq 1.0$ , iteration number represents the diffusion time. (b) The simulation results of 50 iterations when 10% excess  $\text{PbI}_2$  is introduced. (c) The simulation results of 100 iterations when 10% excess  $\text{PbI}_2$  is introduced. (d) The simulation results of 250 iterations when 10% excess  $\text{PbI}_2$  is introduced. (e) The simulation results of 500 iterations when 10% excess  $\text{PbI}_2$  is introduced. (f) The simulation results of 1000 iterations when 10% excess  $\text{PbI}_2$  is introduced. Irregular diffusion is observed.

A more surprising phenomenon is observed when the molar ratio of  $\text{PbI}_2$  and organic halide is set to 1.15:1, as shown in Figure 4. In Figure 4a–f, the number of blue sites is recorded as 9876 for iteration number ( $T$ ) = 1, 9786 for  $T$  = 50, 9659 for  $T$  = 100, 9580 for  $T$  = 250, 9250 for  $T$  = 500, and 8578 for  $T$  = 1000. The curve-fitted line in Figure 5a shows lots of deviation, meaning that the water intrusion is greatly impeded by a large number of halogen bonds, which act as an additional support force of the perovskite structure. As a result, it is harder for the degradation to occur, effectively reducing the number of water paths for diffusion. Thus, the water molecule shows discontinuous motion in the diffusion process, which is attributed to the existence of the many halogen bonds that hinder the degradation. The water molecules now have to take longer paths to find weak sites for the decomposition to occur. Thus, the decomposing rate is greatly reduced, which shows an almost linear change in Figure 5b. A more continuous diffusion is only observed at  $T$  = 1000, successfully extending the lifetime of the perovskite by at least five times compared to Figure 1. Such results demonstrate the great importance of the design of the PSC preparation process, as it proves that the concentration of  $\text{PbI}_2$  needs to reach a threshold, above which a large number of halogen bonds form to withstand the intrusion of water, which increases the lifespan greatly.



**Figure 4.** (a) The simulation results of 1 iteration when 15% excess  $\text{PbI}_2$  is introduced. Blue =  $P: 0-0.3$ ; green =  $P: 0.3-0.6$ ; red =  $P: 0.6-1$ ; and yellow (orange) (within the central box) =  $P \geq 1.0$ , iteration number represents the diffusion time. (b) The simulation results of 50 iterations when 10% excess  $\text{PbI}_2$  is introduced. (c) The simulation results of 100 iterations when 15% excess  $\text{PbI}_2$  is introduced. (d) The simulation results of 250 iterations when 15% excess  $\text{PbI}_2$  is introduced. (e) The simulation results of 500 iterations when 15% excess  $\text{PbI}_2$  is introduced. (f) The simulation results of 1000 iterations when 15% excess  $\text{PbI}_2$  is introduced. Discontinuous diffusion is observed.



**Figure 5.** (a) Recorded number of blue sites (remaining perovskite) for no excess  $\text{PbI}_2$ , at  $T = 1$ ,  $T = 50$ ,  $T = 100$ ,  $T = 250$ ,  $T = 500$  and  $T = 1000$ . The fitted-curve shows an exponential trend, indicating the accelerated degradation. (b) Recorded number of blue sites (remaining perovskite) for 5%, 10%, and 15% excess  $\text{PbI}_2$ , at  $T = 1$ ,  $T = 50$ ,  $T = 100$ ,  $T = 250$ ,  $T = 500$  and  $T = 1000$ . The blue and red fitted-curves show a quasi-exponential trend, with some deviation, indicating the degradation is impeded by the halogen bond. The green fitted-curve cannot match to the green line, suggesting a completely different degradation pattern, due to the presence of a large number of halogen bonds, which almost stops the decomposition.

#### 4. Summary

In conclusion, numerical simulations of well-iterated perovskite solar cell structures were performed to investigate the effect of halogen bonds on their moisture degradation rate, which is the major barrier to commercialization. Irregular diffusion processes are observed after inducing excess  $\text{PbI}_2$ , which passivates the imperfection area in the perovskite and forms halogen bonds with the neighboring organic cations. It is shown that, although

the path update greatly accelerates the diffusion, the presence of halogen bonds could significantly hinder the motion of water, especially at the early stages of the degradation, and the lifetime of the perovskite can, thus, be extended by at least five times. These discoveries help to fight against the instability issues, as reported in the previous experiments, which will, hopefully, provide an ultimate guideline for designing novel PSC devices, and lay down the foundation for the wider PSC community to further explore the detailed physics involved.

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