# Divide-and-conquer DFTB-MD simulations of polaron formation process in a lead halide perovskite material

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In solids, negative or positive charge carriers wear the strutural deformation and form polarons. Polarons play key role in photo-electronic devices, for instance, solar cells. In perovskite solar cells, which are photovoltaic devices constructed by lead halide perovskites (LHPs), extremely long lifetime and diffusion length of charge carriers is observed. In order to elucidate the mechanism underlying these properties, polaron formation mechanism in LHPs needs to be clarified. In particular, there is an open discussion over the role of rotational motion of the organic molecular cations ($CH_3NH_3^+ = MA^+$) incorporated in the LHPs, which might protect the charge carriers from electron–hole recombination. While quantum mechanical (QM) molecular dynamics (MD) is a promising way to unvail the polaron formation process, the spatial size of the polarons, which is estimated at nm scale, is not accessible by conventional first-principles MD technique such as Kohn–Sham density functional theory because of their computational cost. In this work, we employed the divide-and-conquer type density-functional tight-binding (DC-DFTB)[1,2], which is a linear scaling semiempirical quantum chemical calculation method capable of picoseconds MD simulations for systems composed of thousands of atoms. We tracked the polaron formation process in $MAPbI_3$, which is a representative LHP material, by DC-DFTB-MD simulations with the use of a $3.7\,\mathrm{nm} \times 3.7\,\mathrm{nm} \times 5.4\,\mathrm{nm}$ simulation cell (3,072 atoms) to obtain a realistic description of the polaron. The calculations were conducted with DCDFTBMD code[2]. Snapshots of spatial distibutions of the charge carriers are depicted in Figure 1. We found the structural dynamics of not only the $MA^+$ but also the remaining part of the material, $PbI_3^-$, involve the polaron formation. Also, we established that the polaron formation occurs in two distinct steps; the charge localization attributed to the thermal fluctuation of the structure, and the further structural deformation induced by the charge carrier. In addition, in order to provide a hint for the abovementioned hypothesis, that is, importance of the $MA^+$, we evaluated the energetical contribution of the $PbI_3^-$ framework and the $MA^+$. Further details will be presented in the poster.

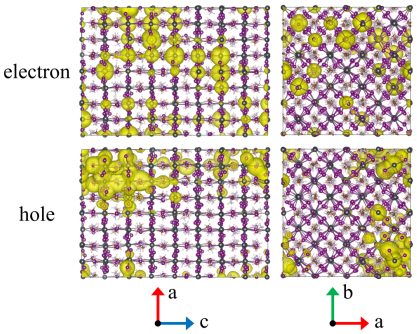


*Figure 1: Snapshots of spatial distribution of negative (upper) and positive (lower) charge carriers.*

**References**

1. H. Nishizawa, Y. Nishimura, M. Kobayashi, S. Irle, and H. Nakai *J. Comput. Chem.* 37, 1983–1992 (2016).
2. Y. Nishimura and H. Nakai *J. Comput. Chem.* 40, 1538–1549 (2019).