

SUPERATOM MOLECULAR ORBITALS OF Li@C₆₀ MONOLAYER

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Superatom molecular orbitals (SAMOs) of highly symmetric C₆₀ molecule have recently attracted significant interest due to delocalized and well-oriented nature of SAMO that allows one potentially to facilitate the utility of these molecules in organic electronics beyond conventional limits. SAMOs of the isolated C₆₀ molecule has been rather widely studied, while the nature of SAMOs in molecular films on substrates has yet to be unraveled, in spite of its importance in a practical application, for instance, in weak electron-phonon interaction responsible for cooling of hot carriers. Moreover, study of endohedral molecules is especially interesting with respect to SAMOs, because endohedral doping lower energy of SAMOs toward the Fermi level. Employing density functional theory (DFT) calculations and scanning tunneling microscopy (STM), we directly demonstrated the spatial and energetic distribution of the delocalized superatom molecular orbitals of Li@C₆₀ and their the wavefunction distributions and electronic features in dependence with the position of Li within the cage and the type of substrate species. Real STM images exhibit isotropic and delocalized nearly free electron like states in Li@C₆₀ islands. The characteristics of SAMOs in terms of shape and energy are quite sensitive to the Li position due to different charge redistributions. The substrate affects the intermolecular distances in the Li@C₆₀ films and modifies the widths and dispersion of the SAMO bands while retaining energetics similar to that of the isolated Li@C₆₀ monolayer. A properly chosen substrate can so be beneficial for Li confinement and SAMO stability reflecting the molecule-substrate interaction and the charge transfer at the interface. The findings provide insight toward the design and engineering of SAMOs of molecular films.