



# Structural effects on the electronic characteristics of intramolecularly intercalated alkali-rubrene complexes



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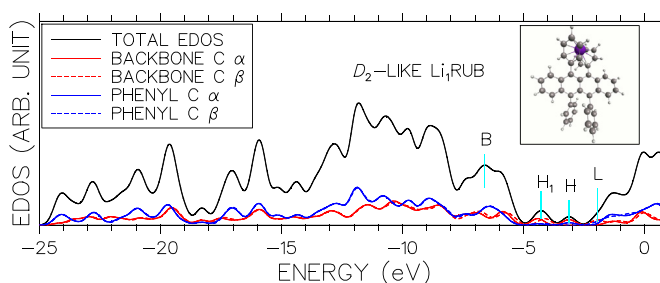
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## HIGHLIGHTS

- Structural effects on the electronic characteristics of alkali-rubrene complexes are studied.
- Minimum-energy isomers of Li- and Na-rubrene are the intramolecularly intercalated structures.
- Carbon 2p orbitals of the intercalated phenyls are promoted to participate in HOMO.
- The unpaired HOMO electron is delocalized over the fused rings of backbone.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The geometric and electronic structures of neutral monolithium- and monosodium-rubrene ( $\text{Li}_1$  Rub and  $\text{Na}_1$  Rub) isomers are investigated and compared with monopotassium-rubrene ( $\text{K}_1$  Rub). Based on the alkali binding site, all isomers of these alkali-rubrene complexes can be subdivided into two types: intramolecularly intercalated and extramolecularly adsorbed. The minimum-energy  $\text{Li}_1$  Rub and  $\text{Na}_1$  Rub are intercalated structures, whereas the minimum-energy  $\text{K}_1$  Rub is adsorbed. The fact that the intercalated  $\text{Li}_1$  Rub and  $\text{Na}_1$  Rub structures are energetically favorable over the adsorbed ones can be explained by two energy rules. First, “double” proximity of the intercalating alkali element to a pair of phenyl side groups enormously reduces the total energy. Second, accommodation of a minuscule intercalant does not significantly deform the carbon frame and, thus, increases the energy only by a small amount. Additionally, the peculiar effects of intramolecular intercalation on the electronic structures of molecules are also studied in this simulation of monoalkali intercalation. In the monoalkali-intercalated rubrene complex, only one of the two pairs of phenyl groups of rubrene is intercalated, intentionally leaving another pair pristine, which facilitates the comparison of electronic structures between the intercalated and pristine pairs of phenyl side groups in a single molecule. The uniformity of chemical environments of the phenyl groups of the intercalated  $\text{Li}_1$  Rub/ $\text{Na}_1$  Rub is deteriorated by the incorporation of the intercalant, and leads to their spectral characteristics in contrast to  $\text{K}_1$  Rub. In particular, the introduction of the intercalant promotes the carbon 2p orbitals of the intercalated phenyl pair to take part in the electronic structures of the HOMO and LUMO peaks of  $\text{Li}_1$  Rub/ $\text{Na}_1$  Rub. The unpaired electron

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in the HOMO is delocalized over the backbone with higher probability of distributing over the central two fused rings than over the outer two.

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## 1. Introduction

Polycyclic aromatic hydrocarbons (PAH) are currently attracting considerable research attention because of their potential applications to organic semiconductive devices [1–5]. Among these types of hydrocarbons, rubrene (5,6,11,12-tetraphenyltetracene,  $C_{42}H_{28}$ ) [6–10] is one of the most intensively studied materials because of its high electron mobility [11,12]. A pristine rubrene molecule has a tetracene-like backbone and four phenyl side groups bonded to the backbone in  $D_2$  or  $C_{2h}$  symmetry [6–8].

Rubrene has broad applications on organic electronic and optoelectronic devices ranging from field-effect transistors [13,14], thin-film transistors [15,16], light-emitting diodes [17,18], to solar cells [19,20]. For device applications, rubrene is often fabricated as thin films with alkali doping [21–24]. Alkali doping significantly modifies the molecular electronic structures as well as the level alignments of the organic materials with metal contacts. Device performances can be improved by properly tuning the alkali doping [25].

Incorporation of alkali metals to rubrene has been achieved by vacuum deposition [26–28] and controlled reduction [29], and studied by the density functional theory (DFT) simulations [27,30,31]. In the present literature about the experimental work on alkali-rubrene, the vacuum deposition methods have been reported for sodium- [26], potassium- [27] and cesium-rubrenes [28], whereas the controlled reduction methods involve lithium-, rubidium-, and cesium-rubrenes [29].

Following the vacuum deposition of rubrene, the alkali metals are evaporated from a getter source to the thin film. The rubrene thin films prepared with this method are most likely amorphous. The alkali-doped rubrene thin films are then investigated with synchrotron radiations to obtain the photoemission spectra (PES) [26–28]. The PES spectra of the alkali-doped rubrene thin films are compared with the energy density-of-states (EDOS) obtained by DFT simulations [32]. Because of the periodic nature of solid-state systems, the density-of-states (DOS) are accounted by the number of states per unit energy per unit crystal volume. The EDOS employed for the molecular systems of this work is slightly different from the DOS of solid-states. The EDOS is the number of states per unit energy per molecule, integration of which over the entire interval of valence band energy is the total number of quantum levels in the valence band.

Because the intermolecular coupling is low for rubrene [33], isolated molecule models are utilized to approximate the alkali-doped amorphous rubrene thin films. Close resemblance between experimental and theoretical spectra has been demonstrated [27,30], justifying the validity of this approach [32].

Controlled reduction methods are also employed to incorporate alkali metals to rubrene. Alkali-rubrene complexes are prepared by the reduction reactions of pristine rubrene with a proper equivalent of alkali metal in solvent such as tetrahydrofuran (THF) and dimethoxyethane (DME). Addition of hexane to the resulting solution produces crystalline precipitations of the solvated alkali-rubrene adducts. The alkali-rubrenes prepared with controlled reduction are supramolecular assemblies of alkali-rubrene, THF/DME, and hexane with complicated coordination environment. Most of the alkali metals are intermolecularly intercalated between

rubrene and other organic molecules. However, at the alkali/rubrene stoichiometric ratio of 4, some lithium and rubidium elements are found to be *intramolecularly* intercalated between a pair of phenyl side groups [29].

Samples of alkali-rubrenes prepared with vacuum deposition and controlled reduction exhibit quite distinct microscopic and macroscopic structures. The former method is more compatible with modern device fabrication technologies [34] than the latter, and will be the main study subject of this work.

To the best of our knowledge, the intramolecular intercalation of alkali to rubrene have not been studied with theory. In order to investigate the effects of the alkali intercalant on the electronic structures of the intercalated pair of phenyl side groups, only one of the two pairs of phenyl groups of rubrene is intercalated, intentionally leaving another pair pristine. This molecular setting facilitates the comparison of the electronic structures between the intercalated and pristine pairs of phenyl groups. As a result, the alkali-rubrene complexes studied in this work will be concentrated on monolithium- and monosodium-rubrene ( $Li_1$  Rub and  $Na_1$  Rub) isomers.

The rubrene chemisorbed by one alkali element can be found in the alkali doping process close to its initial stage. As will be illustrated later in this work, the monoalkali intercalation to a pair of phenyl groups introduces asymmetry to the complex and distorts the molecular structure to some extent. Molecular distortion is known to be inefficient for solid-state packing and, thus, ineffective as an electronic active layer in devices [35]. Doping with monoalkali to rubrene thin films may not be the ideal final stoichiometric composition for electronic applications as far as the molecular structure is concerned. However, monoalkali-doped rubrenes are substances formed in the intermediate phase of heavier doping. Studies of organic materials in this phase contribute to the understanding of the entire doping process.

With the prior simulation methods successfully applied to the monopotassium-rubrene ( $K_1$  Rub) thin films [30], the geometric and electronic structures of  $Li_1$  Rub and  $Na_1$  Rub are explored in this article. It will be shown that, in contrast to  $K_1$  Rub, the minimum-energy isomers of  $Li_1$  Rub and  $Na_1$  Rub are the intramolecularly intercalated structures. To date, the intramolecularly intercalated structures have been experimentally observed in samples prepared by controlled reduction, but not yet, perhaps later, by vacuum deposition. Structural and electronic characteristics of  $Li_1$  Rub and  $Na_1$  Rub isomers will be thoroughly investigated and significant insights on intramolecular intercalation will be presented in this work.

## 2. Computational methods

In the process of vacuum deposition of alkali metals to rubrene thin films, both constituents are neutral in charge. Upon the chemisorption of the alkali metal to rubrene, the valence electron of the alkali element is transferred to the rubrene molecule. As a result, the alkali-rubrene complexes are also neutral. Hence, all DFT simulations of  $Li_1$  Rub and  $Na_1$  Rub isomers are performed with the charge of 0 and the spin multiplicity of 2 in this work.

In the DFT simulations of  $Li_1$  Rub and  $Na_1$  Rub isomers, the alkali-rubrene isomers are formed by introducing a lithium or

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