

## SUMMARY OF Ph.D. DISSERTATION

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<p>Title</p> <p style="text-align: center;">Formation of Large Cluster Anions of Aromatic Hydrocarbons and Size Effect on Their Structures and Electronic States</p>		
<p>Abstract</p> <p>The electronic properties of organic molecules such as aromatic hydrocarbons recently attract considerable attention in organic electronics fields, e.g., organic light-emitting diodes, solar cells, or field-effect transistors, and microscopic understanding of their optical and electric properties in organic molecular crystals is one of the most important challenges. In particular, it is expected that the detailed understanding at the molecular level of aggregation structures and electronic states in organic molecular crystals not only become the basis for design of organic devices, but also provide a point to prompt progress in theoretical chemistry. “Cluster,” which enables us to clearly define number of molecules in molecular aggregation, is expected to become a powerful method to solve such challenges because its electronic state for each size can be observed. However, the previous experimental studies of molecular clusters were obtained as result of limited size range from two to about ten molecules. Drastic increase of number of molecules consisting of a cluster is experimentally indispensable in order to elucidate aggregation structures and electronic states in organic molecular solids. In this thesis, I present two challenges: (1) the establishment of methodology for production of “large” molecular clusters bridging from a molecule to bulk, and (2) the elucidation of correlation between their aggregation structures and electron states using anion photoelectron (PE) spectroscopy.</p> <p>In Chapter 1, research background, motivation, and the content of each chapter in this thesis are described. In Chapter 2, experimental method and quantum chemical calculation are described. On the basis of the background and the new methodology, results in large clusters of aromatic hydrocarbons are mentioned in Chapters 3–6. In Chapters 3–5, production of large cluster anions of oligoacene molecules such as naphthalene, anthracene, and tetracene, and correlation between their electronic states and structures using PE spectroscopy are described. For PE spectra of oligoacene cluster anions, two types of isomers coexist in a larger size range: isomers I and II-1/II-2. Isomer I forms aggregation, in which the neutral molecules is orientated around a monomeric anion core. On the other hand, isomers II-1 and II-2, in which excess electron forms a multimeric anion core, maintain a herringbone-type (crystal-like) structure.</p> <p>In Chapter 3, for cluster anions of alkyl derivatives of anthracene except for their 2-methyl derivatives, no isomers II-1 and II-2 were produced under any experimental conditions because the effective <math>\pi</math>-<math>\pi</math> interactions are substantially hindered within the 2D herringbone layer.</p> <p>In Chapter 4, for related aromatic hydrocarbons of naphthalene such as azulene, no isomers II-1 and II-2 were observed, indicating that a highly anisotropic and symmetric <math>\pi</math>-conjugated molecular framework is an essential factor for the formation of the crystal-like ordered forms (isomers II-1 and II-2).</p> <p>In Chapter 5, aggregation structures of isomer II are presumed from mass and PE spectra of tetracene cluster anions.</p> <p>In Chapter 6, the PE spectra of pyrene cluster anions suggest that the excess electron in (pyrene)<sub>2</sub><sup>-</sup> is delocalized over the two pyrene moieties, whereas in (pyrene)<sub>3-100</sub><sup>-</sup> the excess electron is predominantly localized on a single pyrene molecule.</p> <p>In Chapter 7, the results in this thesis are summarized.</p>		