【Grant-in-Aid for Scientific Research (S)】

Broad Section E

Title of Project： New Main Group Element Chemistry and Materials Science Based on Heavy Aryl Anions

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Keyword：aryl anion, high periodic main group element, aromatic compound

【Purpose and Background of the Research】

Multiple-bond compounds of high periodic main group elements, *that is* "heavy main group elements," have characteristic properties such as their small HOMO-LUMO energy difference. However, they are generally very reactive and readily polymerize. In order to stabilize such compounds, steric protection with bulky substituents and/or electronic perturbations with heteroatom substituents or ligands are required. The necessity of introducing such special substituents has restricted the further application of the excellent properties of "heavy multiple bonds".

We have recently succeeded in the synthesis and isolation of "heavy phenyl anions," in which the anion carbon of the phenyl anion is replaced with Ge or Sn. While they have sufficient properties as aromatic compounds, *i.e.* Ge/Sn-containing multiple bonds, they are able to exist as thermally stable compounds without bulky substituents due to their charge repulsion. We will further develop this discovery as "heavy aryl anion chemistry", extract the difference from carbon analogues, and design and synthesize novel conjugated molecules containing heavy elements. As an ultimate goal, the construction of "heavy graphene" in which some skeletal carbons of graphene are replaced with heavy group 14 elements will be investigated.

【Research Methods】

In this research, we will carry out the studies mainly from the following three viewpoints.

(a) Design of "heavy aryl anion" building blocks having various electronic states and structures: We will develop a new methodology that enables efficient and systematic synthesis of derivatives having (1) various heavy group 14 elements (Si, Ge, Sn, Pb), (2) fused and linked polycyclic rings, (3) heterocycles, and complex systems of (1) to (3).

(b) Determination of the properties of "heavy aryl anions": In "heavy phenyl anions", we have found the divalent character of the central heavy element. This unique property, negligible for the parent phenyl anion, indicates the possibility of molecular transformation different from carbon chemistry, and it is considered to be largely variable depending on the type of substitution elements and ring structures. By systematic understanding based on the results of various spectroscopies, structural analysis, verification of reactivities, and theoretical calculations of the compounds obtained in (a), it leads to molecular design according to desired physical properties and reactivity.

(c) Creation of novel high-order conjugated molecules: By combining the "heavy element chemistry" approach obtained in (a) and (b) with the widely accumulated "carbon chemistry" approach, we will expand the research into higher-order conjugated systems such as "heavy PPV (*p*-phenylene vinylene)" or "heavy aryl anion polymer".

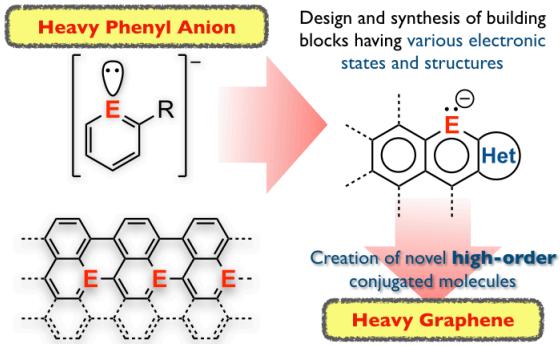

Figure 1. Summary of this research

【Expected Research Achievements and Scientific Significance】

The stabilization methods for highly reactive species of heavy elements have been limited to kinetic stabilization and thermodynamic stabilization. The system in this research may give us a new concept of stabilization, which should be termed as "the third stabilization", completely different from those mentioned above. If this system has generality, great impact and influence will be expected on the development of element chemistry.

【Publications Relevant to the Project】

・"Germabenzenylpotassium: A Germanium Analogue of a Phenyl Anion", Y. Mizuhata, S. Fujimori, T. Sasamori, N. Tokitoh, *Angew. Chem. Int. Ed.* **2017**, *56*, 4588.
・"Stannabenzenylpotassium: The First Isolable Tin-Containing Benzene Derivative", S. Fujimori, Y. Mizuhata, N. Tokitoh, *Chem. Eur. J.* **2018**, *24*, 17039.

【Term of Project】

FY2019-2023

【Budget Allocation】

154,700 Thousand Yen

【Homepage Address and Other Contact Information】

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