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学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Synthesis of Transition Metal Substituted Pentacene Derivatives and Their Application

(遷移金属を置換基にもつペンタセン誘導体の合成及び応用研究)

This Ph.D. thesis consists of five chapters.

Chapter 1: Introduction of synthetic methods for acenes and two dimensional acenes

In this chapter, Mr Wang described the synthetic methods for aceens and 2D acenes. One-dimensional acenes are comprised of the linearly fused benzene rings. On the other hand, two-dimensional acenes are planarly fused benzene rings. Both types are promising π–materials.

Pentacene is a representive 1D acene as organic semiconductors. So far, there are many examples of organic groups substituted peantcene derivatives. The main group metals substituted pentacene have been reported for several examples. However, there is no example of transition metal σ-bond substituted pentacene derivatives. In this work, a variety of Pd or Pt substituted pentacen derivatives was synthesized and isolated successfully. Furthermore, these complexes were applied for introducing substituents into pentacene from both nucleophiles and electrophiles.

As for 2D acenes, graphene ribbons have attracted much attention as next generation semiconductors. Several papers were reported for their synthesis. However, there is no report for pentacene based graphene ribbon. The pentacene oligomers were important precursors of pentacene based graphene ribbon. And formation of dimer is much critical. Therefore, in this work, a series of selective methods for pentacene dimer was developed by use of well-defined transition metal substituted pentacene derivatives. The method is applicable to a series of pentacene oligomers.

Chapter 2: Synthesis and characterization of palladated pentacene derivatives

In this chapter, Mr Wang focused on the synthesis and characterization of palladated pentacene. Oxidative addition of $Pd(PPh_3)_4$ to 6,13-dibromo-5,14-dihydropentacene was followed by aromatization. The corresponding central ring palladated pentacene was obtained as an unexpectedly stable complex. By the ligands exchanged reaction, the PPh_3 ligands could be changed to PMe_3 or PEt_3. After aromatization, the corresponding palladated pentacene with PMe_3 or PEt_3 was prepared successfully. Moreover, a series of dipalladated pentacene complexes and mixed transition metals substituted pentacene complexes were prepared successfully.

The structures of these palladated pentacene derivatives were verified by X-ray analysis. UV-vis absorption and emission spectra of these palladated pentacene derivatives were measured.

Chapter 3: Introduction of substituents into pentacene using palladated pentacene from electrophiles and nucleophiles

In this chapter, a new method was developed for introduction of substituents into pentacene from electrophiles and nucleophiles selectively. For the formation of substituted pentacene derivatives, many methods have been reported. Takahashi's homologation method and coupling method, the substituents come from starting alkynes. As for pentacenequinone method and cross-coupling method, the substituents come from nucleophiles. In this part, introduction of substituents using Pd-substituted pentacenes will be reported. The advantage of this method is the substituents of these pentacene derivatives come from not only nucleophiles but also electrophiles.

Lithiation of palladated pentacene complex with ^{t}BuLi in THF/toluene afforded palladium-lithium reagent in high yield. By using this important intermediate, the reactions with electrophiles were carried out. A series of substituents was introduced into pentacene from electrophiles. After that, the palladium part underwent cross-coupling to introduce substituents from nucleophiles successfully.

Chapter 4: synthesis of pentacene dimer by using palladated pentacene

In this chapter, Mr Wang focused on investigation of the dimerization of pentacene. With the central ring palladated dihydropentacene in hand, the dimerization of it was studied. However, central ring side dimer of pentacene was not obtained by the cross-coupling reaction. Probably the steric hindrance of the central ring was too high. Second ring and terminal ring palladated pentacene derivatives were then prepared and used for dimerization reaction. However, the second ring dimer of pentacene was not obtained due to the bulkiness of two pentacene derivatives. Compared with central ring and second ring palladated pentacenes, the terminal ring palladated pentacene is less bulky. Interestingly, first ring side dimer of pentacene was obtained in high yield under the same reaction conditions.

Chapter 5: selective oligomerization of pentacene derivatives using platinum

In this chapter, a selective oligomerization of pentacene derivatives using platinum was developed. For formation of pentacene based graphene ribbons, the pentacene oligomers were important precursors. In Chapter 4, the dimer of pentacene using first ring palladated pentacene derivative was prepared. However, the substituents of this dimer are opposite. This is because the same side of two pentacene derivatives was coupled in the cross-coupling. In this Chapter, by use of platinated pentacene, a new dimer was obtained. The substituents of this dimer are in the same direction. Furthermore, this method could be developed into a selective oligomerization of pentacene. For example, based on this dimer formation method, a pentacene trimer was prepared successfully. The substituents of three pentacene moieties were aligned in the same direction.