



Syntheses and Functions of Extended -Conjugated Anthracene Derivatives Based on Regioselective Diborylation of Anthracene Derivatives

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学 位 論 文 要 旨

Abstract of Doctoral Thesis

専攻： 光・ナノ物質機能

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Course : Optoelectronics and Nanostructure Science Name : Yuta Takaki

論文題目：位置選択的ジボリル化を基盤とするパイ共役拡張アントラセン誘導体の合成と機能

Title of Thesis : Syntheses and Functions of Extended π -Conjugated Anthracene Derivatives Based on Regioselective Diborylation of Anthracene Derivatives

論文要旨：

Abstract :

The construction and utilization of π -conjugated compounds such as anthracene are among the important subjects of supramolecular chemistry and optoelectronics directed toward materials and life sciences. Notably, the importance and performance of organic semiconductors have increased significantly over the last 30 years. A variety of aromatic compounds for organic semiconductors have extensively been synthesized and studied, wherein it is known that a key to electronic performance is the crystal packing arrangement. In general, high electronic carrier mobility of organic semiconductors requires strong electronic coupling between molecules, which depends on π - π overlap. Anthracene is one of acene compounds, and a variety of anthracene derivatives have been synthesized because of high solubility and stability, compared with tetracene and pentacene. It has been reported that anthracene derivatives as a π -electronic core are useful building blocks for optoelectronics such as fluorescent dyes, organic electroluminescent devices, two-photon absorption dyes, and triplet-triplet annihilation photon upconversion, and for organic semiconductors such as organic field-effect transistors (OFETs) and organic photoconductors, as well as for π -stacking supramolecular architectures. In terms of supramolecular chemistry, in particular self-assembly of π -conjugated macrocycles, the use of anthracene ring is valuable for self-assembly of macrocycle through π - π and CH- π interactions, compared with benzene and naphthalene rings. It is important to introduce functional groups into the anthracene ring at the appropriate positions. Notably, Ir-catalyzed regioselective direct borylation of anthracene is a useful method for functionalization of anthracene ring because the boryl group can be transformed into other functional groups such as halogen and hydroxy groups and can be applied to the Suzuki-Miyaura cross-coupling for the synthesis of π -conjugated molecules. On the background mentioned above, the author started to

study on syntheses and functions of extended π -conjugated anthracene derivatives based on regioselective diborylation of anthracene derivatives. The author's aims of this thesis are to synthesize anthracene-based semiconductors for OFETs with high hole mobility and anthracene-based planar π -conjugated macrocycles directed to self-assembled π -stacked nanofibers (or nanotubes) as optoelectronics materials.

The first three chapters are concerned with the syntheses and properties of extended π -conjugated anthracenes based on regioselective multiple-borylanthracenes directed to organic semiconductors or optoelectronics.

In Chapters 1 and 2, the synthesis of 2,6-bis(4-pentylphenylethynyl)anthracene **1** (Chapter 1) and 2,7-bis(4-pentylphenylethynyl)anthracene **2** (Chapter 2) were achieved. It is described that the balance between good solubility and high crystallinity is an advantageous characteristic of **1** and **2**. Optical properties and crystal packing structures were compared between **1** and **2**. Organic field-effect transistors (OFET) featuring either a vacuum-deposited film or simple drop-cast film of **1** both showed high hole mobilities of 0.94 and 0.63 cm²V⁻¹s⁻¹, respectively.

In Chapter 3, Ir-catalyzed direct tetraborylation of anthracene to give 1,3,5,7-tetrakis(Bpin)anthracene **3** was achieved by using a combination of [Ir(OMe)(COD)]₂ and 3,4,7,8-tetramethyl-1,10-phenanthroline (tmphen) as a catalyst. Compound **3** was applied to the synthesis of 1,3,5,7-tetraarylanthracenes **4** as a new molecular entity. Compounds **4** showed long fluorescence lifetime in the solid state.

The second two chapters are concerned with synthesis and self-assembly of macrocyclic π -conjugated anthracene derivatives **5–7** directed to self-assembled π -stacked nanofibers.

In Chapter 4, the synthesis of cyclic arylene ethynylene hexamers **5a–c**, composed of alternating 2,7-anthrylene ethynylene units and *meta*-phenylene ethynylene units, was achieved based on 2,7-diborylanthracene. Macrocycles **5a–c** show C₃ symmetry and possess a flat and rigid conformation with a large equilateral triangle-like cavity. Macrocycle **5a** self-associates with indefinite-association constant $K_E = 6980 \text{ M}^{-1}$ in CDCl₃ at 303 K. Macrocycles **5a–c** also self-assemble into π -stacked nanofibers in the drop-cast film through π - π stacking interactions between the anthracene-containing macrocyclic aromatic cores and intermolecular van der Waals interactions between the three alkyl chains of **5a–c**.

In Chapter 5, it is described that the Ir-catalyzed direct diborylation of 1,8-disubstituted-anthracenes specifically produce 1,8-disubstituted-3,6-diborylanthracenes. By using 1,8-diaryl-3,6-diborylanthracene (R = C₆H₄-*p*-hexyl), the syntheses of cyclic 2,7-(4,5-diaryl)anthrylene hexamer **6a** and cyclic 2,7-(4,5-diaryl)anthrylene ethynylene hexamer **7a** were achieved. It was confirmed that both anthracene macrocycles self-aggregate through π - π stacking interactions, revealed by the fluorescence spectroscopic study and DLS measurements.