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

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学位論文要約

Summary of Doctoral Thesis

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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

論文要約：
Summary :

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.

Compound numbers in each chapter described below correspond to compound numbers in each chapter in this Doctoral Thesis.

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 Chapter 1, the synthesis and X-ray crystallographic analysis of 2,6-bis(4-pentylphenylethynyl)anthracene (**1**) were achieved. We found that the balance between good solubility and high crystallinity is an advantageous characteristic of **1**. We also found that organic field-effect transistors (OFETs) featuring either a vacuum-deposited film or a simple drop-cast film of **1** both showed high hole mobilities of 0.94 and 0.63 $cm^2\ V^{-1}\ s^{-1}$, respectively. We have demonstrated that (1) the replacement of the double bonds in 2,6-bis[2-(4-pentylphenyl)vinyl]anthracene (**2**) by triple bonds in **1** leads to significant improvement of the solubility of **1**, compared with that of **2**, while maintaining high crystallinity, (2) the crystal packing structure including the dense herringbone packing arrangement of **1** was similar to that of **2**, and (3) the FET performance of the vacuum-deposited film of **1** was comparable to that of **2**. For the OFET devices based on **1**, it should be emphasized that the mobility of the drop-cast film is comparable to that of the vacuum-deposited film. These results suggest that the use of triple bonds in place of double bonds in extended π-conjugated aromatics is a promising approach that can be incorporated into the molecular design of solution-processable organic semiconductors.

In Chapter 2, 2,7-bis(4-pentylphenylethynyl)anthracene (**2**) as a V-shaped regioisomer of 2,6-bis(4-pentylphenylethynyl)anthracene (**1**) was synthesized, and the optical properties and crystal packing structure of **2** were investigated in comparison with **1**. The DTF calculations and UV-vis absorption spectroscopic study indicated that **1** possesses somewhat more extended π-conjugation than **2**. The X-ray crystallographic analysis of single crystals indicated that the crystal packing structure of **2** is similar to that of **1**, namely, a lamella-like layer-by-layer structure consisting of alternate alkyl and bis(phenylethynyl)anthracene layers, and herringbone packing arrangement of bis(phenylethynyl)anthracene moiety. It was found that **2** is slightly more densely packed than **1**.

Studies on OFET properties of **1** and **2** fabricated by edge-casting method, which is one of solution-processed single crystal OFET methods, are in progress in our laboratory.

In Chapter 3, Ir-catalyzed direct tetraborylation of anthracene to give 1,3,5,7-tetrakis[(pinacolato)boryl]anthracene **5** was achieved by using a combination of $[Ir(OMe)(COD)]_2$ and 3,4,7,8-tetramethyl-1,10-phenanthroline (tmphen) as a catalyst. We also revealed the structural properties by X-ray crystallographic analysis and photophysical properties of **5**. Compound **5** serves as a building block for the synthesis of anthracenes with extended π-conjugation at the 1,3,5,7-positions as a new molecular entity. Thus, we synthesized 1,3,5,7-tetraarylanthracenes **7** by the Suzuki–Miyaura coupling reaction of **5** with arylbromide. We also revealed the photophysical properties of **7**. To our knowledge, this manuscript is the first examples for the synthesis of 1,3,5,7-tetraborylanthracene **5** and 1,3,5,7-tetraarylanthracenes **7**. In particular, we found the long fluorescence lifetimes of **7a** ($X = p\text{-}C_6H_{13}$: $\tau = 34.6$ ns) and **7b** ($X = p$-CN: $\tau = 36.4$ ns) in the solid state, compared with those of 2,6,9,10-tetraarylanthracene **8a** ($X = p\text{-}C_6H_{13}$: $\tau = 6.5$ ns) and 2,6-diarylanthracene **9a** ($X = p\text{-}C_6H_{13}$: $\tau = 5.7$ ns).

Studies on the synthesis of anthracene derivatives based on **5** with extended π-conjugation at the 1,3,5,7-positions, and their applications to optoelectronics, are in progress.

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

In Chapter 4, we successfully synthesized cyclic 2,7-anthrylene ethynylene 1,3-phenylene ethynylene trimer **1a**–**c**, namely, cyclic arylene ethynylene hexamers composed of alternating 2,7-anthrylene ethynylene units and *meta*-phenylene ethynylene units. To our knowledge, macrocycle **1** is the first example of a macrocycle containing 2,7-anthrylene ethynylene units. The key for the synthesis of **1a**–**c** is the use of 2,7-diborylanthracene **2** that we developed. Macrocycles **1a**–**c** show C_3 symmetry and possess a flat and rigid conformation with a large equilateral triangle-like cavity. We found that macrocycle **1a** self-associates with indefinite-association constant $K_E = 6980\ M^{-1}$ in $CDCl_3$ at 303 K, as revealed by the concentration dependence and temperature dependence ^1H NMR studies. This K_E value was 116 and 40 times greater than cyclic *meta*-phenylene ethynylene hexamer and cyclic *meta*-phenylene diethynylene hexamer, respectively. This result indicates the enhancement of π–π stacking interactions of **1a** assisted by anthracene rings. We also found the self-associations of **1b** and **1c** by π–π stacking interactions. The fluorescence emission study also supported the π-stacked self-association of **1a**–**c** in solution as well as in the solid state, wherein an excimer emission peak increased with increasing the concentration of **1a**–**c**. We found that macrocycles **1a–c** self-assemble into π-stacked nanofibers in the drop-cast film, as revealed by the SEM images, through π–π stacking interactions between the anthracene-containing macrocyclic aromatic cores and intermolecular van der Waals interactions between the three alkyl chains of **1a–c** with C_3 symmetry. The XRD and GI-XRD studies revealed that **1a** forms a helical π-stacked column with ca. 5.6 molecules per turn through π–π stacking interactions, and the helical π-stacked columns of **1** self-assemble into nanofibers with hexagonal packing structure through intermolecular van der Waals interactions of the three alkyl chains of **1a** with C_3 symmetry.

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 **6**. By using 1,8-diaryl-3,6-diborylanthracene **6a** (R = C_6H_4-*p*-hexyl), the syntheses of cyclic 2,7-(4,5-diaryl)anthrylene hexamer **2a** and cyclic 2,7-(4,5-diaryl)anthrylene ethynylene hexamer **3a** were achieved. To our knowledge, this manuscript is the first examples for the syntheses of **6**, **2**, and **3**. In Chapter 4, we described the synthesis and self-association and photophysical properties of cyclic arylene ethynylene hexamer **1** composed of alternating 2,7-anthrylene ethynylene units and *meta*-phenylene ethynylene units. It is desirable to construct cyclic 2,7-anthrylene hexamer and cyclic 2,7-anthrylene ethynylene hexamer composed of only anthracene units, directed toward materials science such as optoelectronics and organic semiconductors. To allow compatibility between solubility and cofacial π-stacking interactions prerequisite for the formation of nanofiber or nanotube in cyclic 2,7-anthrylene hexamer and cyclic 2,7-anthrylene ethynylene hexamer, we have designed 1,8-disubstituted-3,6-diborylanthracene **6** as a key intermediate for the syntheses of cyclic 2,7-(4,5-disubstituted)anthrylene hexamer **2** and cyclic 2,7-(4,5-disubstituted)anthrylene ethynylene hexamer **3**. In 2,7-anthrylene macrocycles **2** and **3**, substituents at the outward 4,5-positions would enhance the solubility and maintain the inner cavity and would not interfere with cofacial π-stacking interactions of **2** and **3**.

We found the Ir-catalyzed direct diborylation of 1,8-disubstituted-anthracenes **5** with bis(pinacolato)diboron to specifically produce 1,8-disubstituted-3,6-diborylanthracenes **6**. By using 1,8-diaryl-3,6-diborylanthracene **6a** (R = C_6H_4-*p*-hexyl) as a key synthetic intermediate, we achieved the syntheses of cyclic 2,7-(4,5-diaryl)anthrylene hexamer **2a** and cyclic 2,7-(4,5-diaryl)anthrylene ethynylene hexamer **3a** (R = C_6H_4-*p*-hexyl). Based on the fluorescence spectroscopic study and DLS measurements, it was confirmed that (i) both of the anthracene macrocycles **2a** and **3a** self-associate through π–π stacking interactions and (ii) the thermodynamic stability of self-aggregates increases in the order **1** < **2a** < **3a**. This order would be attributed to the enhancement of π–π stacking interactions of **3a** and **2a** assisted by anthracene rings, compared with **1**, and the enhancement of π–π stacking interactions of **3a** with more flat conformation, compared with **2a**.

Based on SEM measurements, it was revealed that **2a** and **3a** form aggregates of very fine needle crystals, but do not self-assemble into nanofibers like **1**, probably because of the rigidity of the *p*-hexylphenyl group as the side chains (R) of **2a** and **3a**. The *p*-hexylphenyl group would enhance intermolecular van der Waals (vdW) interactions between the *p*-hexylphenyl groups, leading to enhancement of densely packing and crystallinity of **3a**. The balance between intermolecular π–π stacking interactions based on the anthracene-based macrocyclic cores and intermolecular vdW interactions based on the side chains (R) would play an important role in the self-assembly of **3** into nanofibers. It is known that ether or ester groups with long alkyl chain or triethylene glycol as side chains are effective for self-assembly of polycyclic aromatic hydrocarbons into nanofibers because these functional groups moderately enhance the flexibility and reduce vdW interactions of side chains. This concept would be very important for the molecular design of **2** and **3** directed to the formation of self-assembled nanofibers.

Studies on the syntheses of cyclic 2,7-(4,5-diaryl)anthrylene hexamers **2** and cyclic 2,7-(4,5-diaryl)anthrylene ethynylene hexamers **3** with various aryl substituents and studies on their self-assembly properties are in progress in our laboratory.