

Summary of Doctoral Dissertation (Doctoral Program (Science/Engineering))

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Structurally Well-defined Polycyclic Aromatic Hydrocarbons Constructed from Pyrene as a Building Block

ピレンを構成単位に用いた構成が明確な多環芳香族炭化水素の合成研究 (英文)

Polycyclic aromatic hydrocarbons (PAHs) are molecules containing two or more fused aromatic rings such as naphthalene, anthracene, phenanthrene and graphene. In recent years, molecular design and synthesis of π -expanded PAHs have been attracting much attention aiming at obtaining molecule based advanced materials such as field effect transistors or molecule based superconductors. Furthermore, synthesis of structurally well-defined polycyclic aromatic hydrocarbons is also a challenge of chemistry. There are two methods are known to synthesize π -expanded PAHs, i) intra-molecular oxidative coupling reaction and ii) photocyclization. Both methods require the corresponding phenylenes as precursors. However the preparation of the phenylene for large PAHs needs a long steps synthesis. When phenylenes were derived from the commercially available small PAH, large PAH will be obtained by short reaction steps. Depending on the type of molecules the content of my thesis is divided into five chapters including the general introduction.

The **second chapter** mainly focused on the study on the syntheses and photophysical properties of pyrene based PAHs. My research group previously reported the oxidation reaction of 1,2-bis(pyrene-2-yl)benzene induce C-C bond formation reaction between the 1-position of two pyrenes and afforded the highly conjugated PAH. To expand this strategy, similar reactions were carried out on 1,2,3-tris(pyrene-yl)benzene and 1,2,4,5-tetrakis(pyrene-2yl)benzene. These molecules were synthesized by Suzuki-Miyaura coupling. To increase the solubility of pyrene, pyrene boronic acid ester having long hydrocarbon chain was used as starting material in this study. The Suzuki-Miyaura coupling reaction of pyrene boronic acid ester with 1,2,4,5-tetrabromobenzene afforded the precursor, 1,2,3,4-tetrakis(pyrene-2-yl)benzene along with the by-product formed by the oxidative homocoupling of pyrene boronic acid ester. The desired PAH, was obtained by intramolecular oxidative coupling in the presence of FeCl_3 . Due to the difficult availability of 1,2,3-tribromobenzene, triflate of 2,6-dibromophenol was used to synthesize 1,2,3-tris(pyrene-yl)benzene.

The absorption spectra of the precursors are superimposed on that of pyrene. Reflecting the expansion of conjugation, bathochromic shifts were observed for dimer, trimer and tetramer comparing with those of precursors. The degrees of the shifts for dimer and tetramer are similar, interestingly, that is larger for trimer. The behaviors of emission spectra are similar, *i.e.*, larger bathochromic shift was observed for trimer. With

an aim to understand the energy level of HOMO and LUMO, electrochemical studies were carried out. In cyclic voltammetry, all these three PAHs showed amphoteric redox behaviors, *i.e.*, both oxidation and reduction processes in electrochemistry. The first reversible oxidation process of dimer was found at +0.75V (vs Fc/Fc⁺) and a reversible reduction process at -2.10V. Similarly, tetramer showed a quasi-reversible oxidation process at +0.61V and a reversible reduction process at -2.18V. But for trimer, the first oxidation process was shifted negatively to +0.56V and first reversible reduction at -2.05V indicating smaller HOMO-LUMO gap of trimer than that of dimer and tetramer. The energy levels of the molecules were confirmed by the density functional theory (DFT) calculation (B3LYP, 6-31G, d). The energy of HOMO for trimer is higher than dimer and tetramer due to the anti-bonding interaction between three pyrenes. On the other hand, LUMO energy is lower for trimer due to the bonding interaction among pyrenes. The corresponding smaller HOMO-LUMO gap for trimer was reflected in absorption, emission, and cyclic voltammetry. Additionally, it was observed that, sequential conjugation like trimer is needed to reduce the HOMO-LUMO gap.

The **third chapter** describes about the synthesis of thiophene annulated pyrene based polycyclic aromatic hydrocarbon and their photophysical properties. To improve properties of molecules, annulated benzene was modified with thiophene. Thiophene is one of the most important key molecules in interdisciplinary science. Therefore, several specific properties attributable to thiophene would be expected in pyrene-based PAHs. Two different targets were designed using the 2,3 and 3,4 position of thiophene and denoted by 2,3-isomer and 3,4 isomer respectively. The Suzuki-Miyaura coupling reaction of pyrene boronic acid ester and the commercially available 2,3-dibromothiophene yielded the intermediate which was converted to target 2,3-isomer by the treatment with FeCl₃(86%). Similar procedure was applied for 3,4-isomer. Though the yield of the precursors was comparable, the oxidation behavior of 3,4-isomer was quite different. A quick termination gave only 11% corrective yield. This phenomenon can be explained by the contribution of the *ortho*-quinoid structure like unstable benzo[*c*]thiophene which results the high reactivity.

The absorption and emission spectrum and the electrochemical behavior of 2,3-isomer and 3,4-isomer are very similar to those of the benzene annulated dimer. The molecular structure of 2,3-isomer revealed by single crystal X-ray diffraction shows the disorder in the thiophene moiety. The pentacene moiety of 2,3-isomer induce helical structure and the dihedral angle of the pyrene moieties is 40.37°. Because of the helical structure of 2,3-isomer, optical resolution was performed using chiral column in high performance liquid chromatography. Two well separated peaks attributable to the *P*- and *M*-isomer. The circular dichroism spectra of the separated enantiomers of 2,3-isomer shows the mirror image spectra. Racemization of the enantiomers was occurred at room temperature with in very short time.

The **fourth chapter** discuss about the synthesis, photophysical and thermal behavior of

3,3',5,5'-tetrapyrenyldiphenoquinone. Functionalization of hydroxyl group is enable to produce many organic molecules. For example, oxidation of 2,6-diphenyl phenol forms diphenoquinone along with benzoquinone. Using this idea, 2,6-bis(pyrene-2-yl)phenol was prepared by the Suzuki-Miyaura coupling reaction and the subsequent deprotection reaction. Oxidation reaction of 2,6-bis(pyrene-2-yl)phenol with PbO_2 in acetic acid afforded tetrapyrenyldiphenoquinone along with dipyrenylbenzoquinone. The absorption spectra of tetrapyrenyl diphenoquinone showed a band at 537 nm which was shifted to red region comparing with the reference molecule tetraphenyl diphenoquinone (483 nm) or that of dipyrenylbenzoquinone (432 nm). The electrochemical studies, showed two reversible reduction process at -0.56 and -0.85 V and an irreversible oxidation process at +0.75V for tetrapyrenyldiphenoquinone. The reduction process were positively shifted compare to that of tetraphenyldiphenoquinone, -0.65 and -0.92 V, respectively. During the melting point measurement, the deep color of tetrapyrenyldiphenoquinone faded. This behavior is not a decomposition of the molecule. TLC analysis revealed that three colorless product were formed after melting of tetrapyrenyldiphenoquinone. All the spectroscopic studies suggest that these products are hydroquinone and two type of pyrene annulated furan, *i.e.*, bisfuran and monofuran derivative. The thermally excited triplet state of tetrapyrenyldiphenoquinone might participate this reaction because triplate state of diphenoquinone is easily obtained by thermally. Biradical character of triplet state attack to *ortho* position of arylbiphenoquinone.

The **fifth chapter**, focus on the synthesis of extended quinone, *i.e.*, tetrapheylterphenyloquinone and comparison of its properties with tetraphenyldiphenoquinone. The synthesis of the desired tetraphenyl terphenyloquinone was started from a simple molecule 2,6-diphenylphol which was converted to boronic acid ester by a series of reaction such as bromination, protection of hydroxyl group and Ir-catalyzed borylation. The Suzuki-Miyaura coupling reaction of bornicacid ester with 1,4-diiodobenzene and subsequent deprotection reaction yielded the important intermediate corresponding hydroquinone. The oxidation of hydroquinone with PbO_2 in benzene afforded the target terphenylquinone. In absorption spectra, the band for $\pi-\pi^*$ transition was found at 603 nm which has a bathochromic shift as well as hyperchromic effect compare to diphenoquinone. In electrochemistry, positively shifted two reversible reduction process at -0.49 and -0.57 V were closer as the distance between the two reaction centers increases. Heating the sample above the meting point, it converted to three compounds, *i.e.*, bisfuran, monofuran and hydroquinone. Differential scanning colorimetry also confirms this behavior.

In conclusion, it can be stated that the photophysical properties of PAHs including UV-Vis, fluorescence, and cyclic voltammetry indicates that the properties are greatly affected by the increasing the number of benzene ring, *i.e.*, expansion of conjugation. But for further smaller HOMO-LUMO gap, a sequential conjugation is more effective that isolated conjugation. Similar trends also observed in pyrene substituted diphenoquinone.