

## 学位論文題名

Zirconium-Mediated Novel Synthesis and Properties  
of Thiophene-Fused Acene Derivatives

(ジルコニウムを用いたチオフエン縮合型アセン類の新規合成とその性質)

## 学位論文内容の要旨

## Introduction

Thiophene-fused acene (TFA) derivatives are highlighted as promising candidates for organic semiconductors nowadays.<sup>1</sup> It is highly desirable for a synthetic method of TFA to be widely applicable for a series of derivatization. To achieve such method, this work has focused on the following two points: (1) broad diversity for introducing substituents, (2) easy access for construction of various TFA skeletons. So far, our group has reported two synthetic methods of substituted acenes based on zirconium-mediated reactions: homologation method and coupling method.<sup>2,3</sup> Among them, the coupling reaction is quite hopeful for the purpose mentioned above. Numbers and types of the substituents can be controlled by the choice of the starting acetylene compounds. Moreover, the TFA skeletons can also be controlled by changing the coupling partner, halothiophenes.

In this research, variously substituted TFAs were synthesized by the zirconium-mediated coupling reaction. Moreover, the photophysical and electronic properties were also investigated to reveal the effects of introduced substituents on their properties.

**1. Zirconium-mediated synthesis of substituted thiophene-fused acenes with various skeletons.**

To develop the novel synthetic method of TFA with wide diversity, the reaction conditions of the coupling of 2,3-dihalothiophene with zirconacyclopentadiene was optimized.

For effective coupling, employment of 2,3-diiodothiophene was found to be essential. In the coupling reaction of monocyclic zirconacyclopentadiene with 3-bromo-2-iodothiophene, the major product was butadienylthiophene. On the other hand, employment of 2,3-diiodothiophene dramatically improved the yield of desired benzothiophene.

Thus optimized coupling reaction was applied for synthesis of a series of anthra[*b*]thiophenes. Tricyclic zirconacyclopentadienes were prepared from the corresponding diynes, and reacted with 2,3-diiodothiophene to afford the corresponding dihydroanthra[*b*]thiophenes in good yields. Subsequently, these were aromatized by DDQ to furnish the desired anthra[*b*]thiophenes in high yields. These results clearly exhibited the wide applicability of the present method for synthesis of variously substituted anthra[*b*]thiophenes. It is worth mentioned that silyl-substituted zirconacycle did react with 2,3-diiodothiophene, since no coupling products were obtained from the reaction of disilyl-substituted zirconacyclopentadienes with diiodobenzene under the same conditions.

By changing the starting diyne, the method was applied for synthesis of naphtho[*b*]dithiophene. Zirconium-mediated coupling of 2,3-bis(propargyl)thiophene with 2,3-diiodothiophene and succeeding DDQ aromatization afforded naphtho[*b*]dithiophene as a mixture of regio isomers. Furthermore, double coupling with tetraiodothiophene was also possible to furnish dianthra[*b*]thiophene from the reaction of zirconacycle with tetraiodothiophene.

It is worth noting that the present coupling method was applicable for synthesis of anthra[*c*]thiophene derivatives by using 3,4-diiodothiophene. To our best knowledge, this is the first example of anthra[*c*]thiophene derivatives. Although the highly extended quinoidal structure of anthra[*c*]thiophene seemed to be too reactive to isolate, these have sufficient thermal stability in both solid and solution states.

As demonstrated here, widely applicable synthetic method of TFA was realized by zirconium-mediated coupling reactions, which can provide a series of TFAs having variety of substituents and skeletons.

## **2. Introduction of various substituents after the formation of thiophene-fused acene skeletons.**

For further development of the zirconium-mediated coupling for synthesis of TFA derivatives, introduction of substituents after construction of TFA skeletons was examined by two strategies as mentioned below.

With TMS-substituted anthrathiophene, further derivatization was carried out by ICl iodination and palladium-catalyzed cross-coupling reactions. These results clearly exhibited the wide applicability of the present method for introduction of various substituents on the acene skeletons.

Substituents can also be introduced via the corresponding quinone intermediate. Oxidation of dihydroanthrathiophene and dihydronaphthodithiophene provided the corresponding quinones, respectively. When the quinone was treated with phenyllithium followed by reductions, tetraphenyl-substituted anthrathiophene and naphthodithiophene were obtained. Instead of phenyl group, *p*-methoxyphenyl, *p*-trifluoromethylphenyl, and alkynyl groups were also introduced.

## **3. Photophysical and electronic properties of thiophene-fused acene derivatives.**

Photophysical properties of TFAs were studied from absorption spectra, and investigated the relationship with the structures. A variety of substituents can influence the absorption maxima. Different skeletons also showed diversity in photophysical properties. Especially the absorption band of anthra[*c*]thiophene was observed at much longer wavelength region compared with the others. This is due to its quinoidal structure.

Electronic properties of TFAs were also studied from cyclic voltammetry. The HOMO and LUMO levels of TFAs were strongly affected by skeletons and introduced substituents. Alkyl, phenyl, and TMS groups increase the HOMO levels and decrease the LUMO levels, while alkynyl and iodine groups decrease both of the HOMO and LUMO levels. Compared with anthra[*b*]thiophene skeleton, other skeletons also gave strong influence on the electronic properties. Dianthra[*b*]thiophene and anthra[*c*]thiophene have higher HOMO and lower LUMO levels, whereas, naphtho[*b*]dithiophene has lower HOMO and higher LUMO levels.

## **4. Molecular orientation of thiophene-fused acene derivatives.**

Molecular orientation and arrangement in the solid state has a crucial role to determine electronic performances of the organic molecular solid. Generally, proper choice of substituents on the component molecules is an important key factor for controlling the orientation and arrangement. In this work, organic thin films of two anthrathiophene derivatives were analyzed by NEXAFS (Near-Edge X-ray Absorption Fine Structure) spectroscopy. A molecule can absorb certain energy of soft X-ray, and the absorption intensity is dependent on the incident angle of the irradiation. Analyses of the incident-angle-dependence can provide information on the orientations of vectors of  $\sigma^*$ - and  $\pi^*$ -orbitals of the molecule on the substrate.

Thin films of hexapropylanthra[*b*]thiophene and dipropylanthra[*b*]thiophene were fabricated on silicon wafer by vacuum deposition or casting from toluene solution and annealed below their melting points. It was found that in the thin film of hexapropylanthra[*b*]thiophene the molecules were well-ordered in plane-on arrangement, and the angle of the substrate surface to molecular plane was estimated as 78 ° from the intensity dependence on the incident angles of X-ray. While in the film of dipropylanthra[*b*]thiophene, random molecules were observed. So it was found that the difference in the substitution patterns on the TFA skeletons strongly affected the molecular orientation in the solid states.

## **Conclusion**

In this work, an efficient method for the synthesis of substituted TFA derivatives was developed. Construction of TFA was achieved by a zirconium-mediated coupling reaction. The patterns of substitution and the skeletons can be well controlled by this method, which enable us to synthesize a series of TFA derivatives. In addition, substituent and skeleton effects on photophysical and electronic properties of TFA were investigated

by UV-vis absorption, cyclic voltammetry, and NEXAFS spectroscopy. These results promisingly showed significant effects of their physical properties on the substitution and skeleton patterns.

#### References

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# 学位論文審査の要旨

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## 学 位 論 文 題 名

### Zirconium-Mediated Novel Synthesis and Properties of Thiophene-Fused Acene Derivatives

(ジルコニウムを用いたチオフエン縮合型アセン類の新規合成とその性質)

倪陽氏の Zirconium-Mediated Novel Synthesis and Properties of Thiophene-Fused Acene Derivatives (ジルコニウムを用いたチオフエン縮合型アセン類の新規合成とその性質) と題された博士論文は、序論、4 章からなる本論、および結論の 6 章からなる。

序論では、本研究の着想に至る経緯について述べている。チオフエンが縮環したアセン類は近年、有機半導体材料として非常に注目されている。そのような化合物の合成法としては、幅広い誘導化が可能な方法が強く望まれる。倪陽氏の所属する研究室ではこれまでに、ジルコニウムを用いた多置換アセン類の合成法を数多く報告しているが、これらはチオフエン縮環アセン類の合成にも適用できると考え研究に着手した。

第 1 章では、本研究の主題となるカップリング反応について述べている。種々の条件検討の結果、ジルコナシクロペンタジエンに対しジヨードチオフエンを加えると、望むカップリング反応が高収率で進行することが見出され、それを種々の基質に適用することで一連の置換基、および骨格を有するチオフエン縮環アセン類の合成がなされている。これにより、これまでに合成例のないジアントラチオフエン、およびアントラ[c]チオフエンの合成にも成功している。

第 2 章では、チオフエン縮環アセン骨格への置換基導入法について述べている。第 1 章の方法では、導入される置換基は出発物の段階で決まっていたが、本章の方法では骨格を構築後に置換基の導入を行うことができ、幅広い誘導化に適した方法となっている。1 つ目の方法はシリル基を足掛けとする方法である。まず、シリル基を導入したアセン骨格を構築し、そのシリル基をヨウ素に置換した後、クロスカップリング反応を適用することで種々の置換基を導入する方法である。2 つ目の方法は、アセン骨格構築後にキノン中間体へと変換し、そのカルボニル基を足掛けとして置換基を導入する方法である。この方法を用いれば、有機半導体材料として特異な性質を持つルブレノと同様の置換パターンを有するテトラフェニルアントラチオフエンの構築も行うことができる。以上の 2 種類の方法によって、合成できる置換パターンを大幅に広げること成功している。

第 3 章では、前 2 章で得られたチオフエン縮環アセンの物理的、および電気的性質につい

て述べられている。化合物の性質は、吸収-発光スペクトルとサイクリックボルタンメトリーから測定されており、置換基や骨格の違いがもたらす変化について考察している。特に、置換基の違いにより HOMO、および LUMO のエネルギー準位は顕著な変化を示し、それらは骨格の違いによっても変化した。これらデータは、チオフェン縮環アセンの物性を制御する際の指針となる情報として大変重要である。

第 4 章では、置換アントラチオフェン分子の固体薄膜中での配列様式を、NEXAFS を用いて行った結果について述べている。この測定には、プロピル基が 2 つ置換したアントラチオフェンと 6 つ置換したものの 2 種類が用いられている。それぞれから作成した薄膜の NEXAFS 測定の結果、プロピル基が 6 つ置換した誘導体では、分子がシリコン基板に対して立った状態で配列していることが明らかとなった。さらにその配列には、成膜後のアニーリングが重要であることもわかった。これに対し、プロピル基が 2 つだけ置換した誘導体では、アニーリングの有無に関わらず分子が配列した様子は観測されず、完全なアモルファス状態の薄膜であることが示唆された。このように、同一の骨格を持つ分子でその置換様式から固体中の分子配列が顕著に変化する例はこれまでに報告例がなく、大変興味深い実験結果である。

最終章は、上記の内容を簡潔にまとめて本論文を閉じている。

以上のように本論文では、ジルコニウムを用いたチオフェン縮環アセンの新規合成法の開発に始まり、さらにそれを発展させることで種々の誘導体の合成を可能にし、これまでに合成例のない骨格の分子の合成をも可能とした。さらに、それら合成した分子の物理的性質についても詳細に検討を行い、置換基や骨格の違いが及ぼす影響について考察されている。そして、固体薄膜中での分子配列の観測では、置換基の違いにより分子が配列する例が初めて見出されている。以上の内容は、有機半導体分野での注目に値する内容であり、今後のこの分野の発展に対して大きく貢献するものである。以上の点から、本論文は博士の学位に十分に値する内容であると判断した。