

論文 / 著書情報
Article / Book Information

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種別(和文)	論文要旨
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(博士課程)
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論文要旨

THESIS SUMMARY

専攻:	物質電子化学	専攻
Department of		
学生氏名:	Leung King Chi	
Student's Name		

申請学位(専攻分野):	博士	(理学)
Academic Degree Requested	Doctor of	
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Academic Advisor(main)		
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Academic Advisor(sub)		

要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words)

This thesis entitled "Development of Functional Molecular Systems by Structurally Elaborated Triptycenes" consists of six chapters and describes the development of various functional molecular systems using 1,8,10,13-substituted triptycenes as a fundamental building block. This thesis provides new aspects of triptycene, a well-known rigid propeller-shaped molecule, for the applications to semiconducting organic thin films, catalytic system, and self-assembled nanostructures.

Chapter 1, General Introduction. Because of the unique structural properties of triptycene, along with its long history of synthetic diversification, a large number of applications have been proposed in chemistry and materials science. In this introduction section the history of synthesis and diversification, potential applications of structurally elaborated triptycenes are described.

Chapter 2, Triptycene-Based Supramolecular Scaffold for Tailoring the Two-Dimensional Arrays of Fullerene into Organic Thin Film. Our group have reported that the remarkable self-assembling properties of the paraffinic tripodal triptycenes enable the spontaneous formation of thin films with a completely oriented "2D hexagonal + 1D lamellar" structure. Based on this previous finding, a tripodal triptycene-based supramolecular scaffold for tailoring the 2D assembly of functional molecular units into organic thin films has been developed. The building block of the supramolecular scaffold consists of newly designed tripodal triptycenes, which carry a terminal alkyne unit at the bridgehead position for covalent modifications. The supramolecular scaffold can be applied to controlled assembly of functional molecular units with a diameter as large as approximately 1 nm such as C₆₀ unit. Indeed, a C₆₀-appended tripodal triptycene carrying very flexible side chains that allow reordering of the resulting assembly affords a thin film with a highly ordered and oriented "2D + 1D" structure on solid substrates, where the C₆₀ units are densely clustered two dimensionally. This thin film was found to exhibit anisotropic conducting properties. The triptycene-based supramolecular scaffold is capable of directing functional molecular units to assemble into a highly oriented anisotropic 2D structure that is compatible with the geometry of substrate surfaces. The present approach may contribute to the design of high-performance organic thin films with anisotropic functionalities.

Chapter 3, Triptycene-Based Supramolecular Scaffold for Tailoring the Two-Dimensional Arrays of *p*-Type Semiconducting Molecular Units into Organic Thin Film. With comprehensive investigations of the triptycene-based supramolecular scaffold for tailoring the 2D arrays of fullerene into organic thin films as investigated in Chapter 2, a further demonstration through functionalization of a *p*-type semiconducting unit, benzo[thieno[3,2-b][1]benzothiophene (BTBT), on the tripodal triptycene molecular motif is described in this chapter. The BTBT-appended tripodal triptycene affords a thin film with a structural order essentially identical to that observed for C₆₀-appended tripodal triptycene.

Chapter 4, Unidirectional Alignment of Supramolecular Polymer Tailored by Triptycene-Based Supramolecular Scaffold. Macroscopic alignment of supramolecular polymers have been developed as one of the simple but practically important methods for providing anisotropic soft materials. This chapter describes the formation of a self-assembled nanofiber from an amphiphilic 1,8-substituted triptycene in aqueous media. High-resolution electronic microscopy and synchrotron X-ray diffractometry (XRD) of a nanofiber formed in a 5.0 weight% aqueous solution revealed orthorhombic packing of the triptycene molecules. The nanofibers can be aligned by a shear-flow method to afford a macroscopic string of aligned nanofibers. The detailed XRD analysis of the macroscopic string indicated the formation of an orthorhombic packing structure essentially identical to that observed for the nanofiber obtained from a 5.0 weight% aqueous solution of 1,8-substituted triptycene. The clear structural correlation between individual nanofibers in solution and unidirectionally aligned nanofibers in a string, represents that the present approach may serve as useful scaffolds for integrating functional molecular units and, in turn, for the development of anisotropic soft materials.

Chapter 5, Development of a Rigid Bulky Monophosphine Ligand from Asymmetrically Substituted Triptycene Skeleton. This chapter describes the development of a rigid, bulky, and chiral monophosphine ligand based on 1,8-substituted triptycene. The newly designed triptycene monophosphine ligand (TripPhos) exhibits high catalytic activity in palladium-mediated organic transformations. For instance, TripPhos serves as an air/moisture stable ligand for the palladium-catalyzed Suzuki-Miyaura cross-couplings of aryl bromides and arylboronic acids, where only small amount of Pd(OAc)₂ (5–10 mol-ppm) and TripPhos (two equivalents for Pd) under aerobic atmosphere enables the formation of the corresponding biaryls in excellent isolated yield with a high turnover number. The structural information about the coordination manner of TripPhos to Pd was obtained by single-crystal X-ray crystallography. The enantiomerically pure (+)-TripPhos shows good asymmetric catalytic activity and enantioselectivity in palladium-catalyzed hydrosilylation.

Chapter 6, General Conclusion. This chapter summarizes the studies on the structurally elaborated triptycenes for (1) the first supramolecular scaffold to tailor 2D assembly of molecular units into thin films, (2) the first triptycene-based supramolecular polymer with macroscopic unidirectional alignment, and (3) the first catalytic system using 1,8-substituted triptycene monophosphine ligand. This chapter also includes the conclusions of this doctoral thesis and scopes of the related works.

備考: 論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note: Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1copy of 800 Words (English).

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