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研究課題名(和文) Iron-catalyzed Activation of Unreactive Bonds for Organic Materials Synthesis

研究課題名(英文) Iron-catalyzed Activation of Unreactive Bonds for Organic Materials Synthesis

研究代表者

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研究成果の概要(和文)：この研究プロジェクトを通じて、持続可能で経済的な鉄ベースの触媒を使用して有機電子材料にアクセスする合成方法が開発されました。太陽電池および発光ダイオード用の新しい有機光電子材料が開発されました。

チオフェンベースの半導体ポリマーは、安価な試薬を使用した鉄触媒チエニルC-H / C-Hカップリングを使用して製造され、高い持続可能性と経済的メリットのある重合方法を提供します。鉄触媒によるワンポットタンデム環化反応は、剛直な炭素架橋アリレン-ビニレン材料の合成のために開発されました。発光材料に加えて、近赤外光検出器用の非フルラーレンアクセプター材料は、この鉄触媒による環化法を使用して開発されました。

研究成果の学術的意義や社会的意義

鉄を触媒として有機電子材料を作ることのメリットは、現代の化学合成に求められる環境的、持続可能、経済的問題のために顕著です。このプロジェクトの結果は、触媒作用として豊富な鉄塩を使用して新しい電子材料を合成する方法を提供し、有機金属化学と触媒作用の新しい知識を提供します。新しく開発された鉄触媒を使用することによる材料アクセスは、太陽電池、光検出器、および発光のための効率的な材料として発見されました。これらの鉄触媒プロセスは、持続不可能な資源への依存を回避し、有機電子材料の製造コストを削減するために、将来の産業用途に役立つ可能性があります。

研究成果の概要(英文)：Through this research project, synthetic methods to access organic electronic materials using sustainable and economic iron based catalysts were developed. New organic optoelectronic materials for solar cells and light emitting diodes were developed.

Thiophene-based semiconductive polymers were produced by using iron-catalyzed thieryl C-H/C-H coupling using cheap reagents, offering a polymerization method of high sustainability and economic merits. New polymers made by iron-catalysis were found as highly efficient hole transporting to enable high performance perovskite solar cells. An iron-catalyzed one-pot tandem cyclization reaction was developed for synthesis of rigid carbon-bridged arylene-vinylene materials. Beside emissive materials, non-fullerene acceptor materials for near infrared photodetector was developed by using the new ladder molecule accessed by this iron-catalyzed tandem cyclization method.

研究分野：有機合成化学、有機材料化学

キーワード：iron-catalysis C-H activation polymerization perovskite solar cells tandem cyclization non-fullerene acceptor photodetector

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様式 C-19、F-19-1、Z-19、CK-19(共通)

1. 研究開始当初の背景

As the most abundant metal on the Earth, iron has merits of use as catalyst for synthesis of organic electronic materials, such as low cost, low toxicity, and high sustainability, which ideally conforms the spirit of sustainable development goals. The weak interaction of d^5 -Fe(III), the most stable valence of iron, with delocalized π -system in organic materials also facilitates removal of this metal from final products, which is crucial for materials purity and quality. However, synthesis of organic electronic materials so far mostly relies on using precious metals such as palladium and rhodium as catalysts. The prices of those precious metals kept on increasing in recent years due to their non-renewable nature and various geopolitical issues. To develop iron-catalyzed synthetic methodology for organic electronic materials has advantages in both sustainability and economy.

2. 研究の目的

The purpose of this research project is to develop new organic electronic materials and their low-cost production methods using iron catalysis. In this research project, we targeted two types of iron-catalyzed transformations for synthesis of both thiophene based dimeric and polymeric donor materials, and narrow band gap π -materials incorporating 1,4-dihydropentalene skeleton. The iron-catalyzed methods will be easily scalable and are of low cost. These materials made by the iron-catalyzed transformations are expected to be applicable in solar cells, light emitting diodes, and organic photodetectors to have their applications in our society. Besides these plans, we will also explore new reactivity of organoiron and develop novel conjugated molecules to understand their optoelectronic properties.

3. 研究の方法

Two types of iron-catalyzed transformations for synthesis of 1) thiophene based oligomeric and polymeric donor materials and 2) narrow band gap π -materials incorporating 1,4-dihydropentalene skeleton are planned to achieve the expected targets of this research. In part 1, to solve the problem in thiophene-based oligomeric and polymeric materials synthesis, we hypothesized that an iron(III) salt in combination with tridentate phosphine ligand and AlMe_3 as base selectively cleaves thienyl C-H bond at C2 position and allows regioselective thienyl-thienyl coupling of high efficiency using a mild oxidant for catalyst turnover. The compatibility of functional units commonly found in optoelectronic materials will be focused. New polymers synthesized using iron-catalyzed polycondensation will be tested as hole transporting materials in perovskite solar cells. In part 2, carbon bridging in a form of a strained 1,4-dihydropentalene framework is known as an effective strategy for flattening and stabilizing oligophenylenevinylene systems for development of optoelectronic materials. However, there lacks efficient and flexible methods for making such a

strained ring system. We conceived an iron-catalyzed single-pot tandem cyclization of a diarylacetylene to a strained 1,4-dihydropentalene framework containing two carbon bridges. The synthesis will be developed using inexpensive reagents for low-cost production of these materials. The new method are expected to provide access not only to a variety of substituted indeno[2,1-*a*]indenes with exceptional fluorescence properties, but also to their thiophene congeners, 4,9-dihydrobenzo[4,5]pentaleno[1,2-*b*]thiophene (**CPTV**) and 4,8-dihydropentaleno[1,2-*b*:4,5-*b'*]dithiophenes (**CTV**). These molecules will be developed as donor units in narrow-band-gap non-fullerene acceptors for application in near IR photodetector devices.

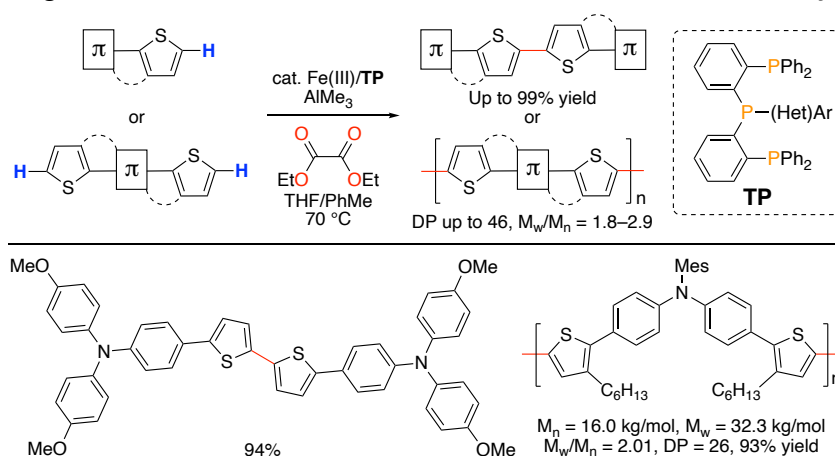
4. 研究成果

Part 1. Iron-catalyzed Regioselective Thienyl C-H/C-H Coupling and Polycondensation

Doba, T.; Ilies, L.; Sato, W.; Shang, R.*; Nakamura, E.* *Nat. Catal.* **2021**, *4*, 631–638

Lin, H.-S.; Doba, T.; Sato, W.; Matsuo, Y.*; Shang, R.*; Nakamura, E.* *Angew. Chem. Int. Ed.* **2022**, *61*, e202203949

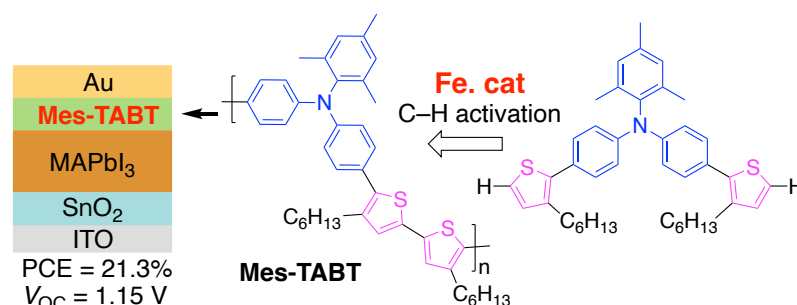
Thienyl-thienyl coupling with regioselectivity control is arguably one of the most important reactions for organic π -electronic materials science as evidenced by a diversity of small molecular, oligomeric, and polymeric semi-conductive materials containing thiophene-thiophene linkage. This transformation is ideally achieved through direct C-H/C-H coupling. However, direct transition-metal-



catalyzed regioselective oxidative C–H/C–H coupling conditions are hardly compatible for various π -units of importance in optoelectronic materials sciences especially for donor materials because these π -units are not redox innocent that interferes an oxidative catalytic cycle, and the catalyst efficacy are hardly sufficient enough to enable direct C–H/C–H polymerization of these π -units to achieve the “holy grail” in synthesis of optoelectronic polymer. We found that an iron(III) salt in combination with tridentate phosphine ligand and trimethylaluminum as base selectively cleaves thienyl C–H bond at C2 position and allows regioselective thienyl-thienyl coupling of high efficiency using a very mild oxalate ester as oxidant for catalyst turnover. The reaction is compatible with various π -units generally found in optoelectronic materials and is

accelerated by ligand optimization to allow C–H/C–H polycondensation to allow synthesis of various small molecular, oligomeric and polymeric semiconductive materials of importance in energy device applications. The work presented herein shows the utilization of the most abundant two metals on earth as tools for the synthesis of conjugated small molecular, oligomeric, and polymeric π -materials of importance in energy device applications, and indicates that iron-catalyzed C–H activation found its advantages and promising future applicability for the related synthetic applications in π -conjugated electronic materials.

Polymer hole-transporting materials (HTMs) are known for their better film stability and processability compared with small molecule HTMs for fabrication of highly



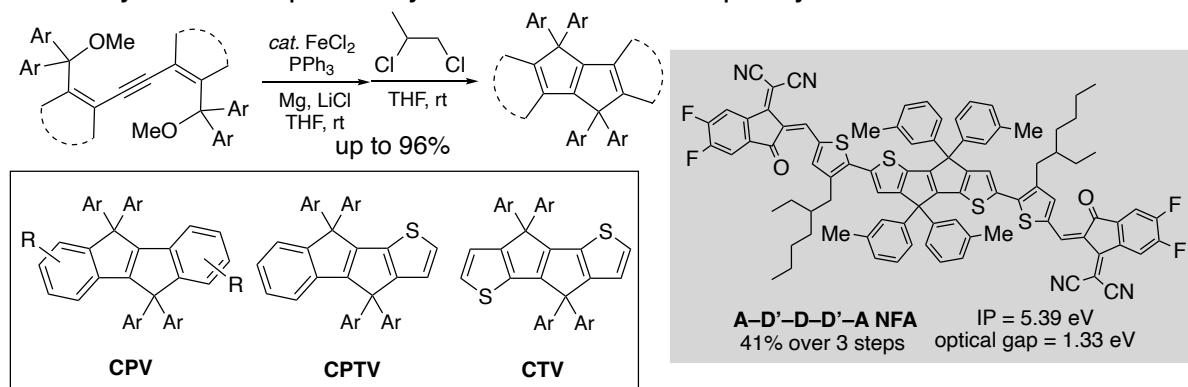
efficient and stable electronic devices. However, complicated synthetic procedures for polymerization and high production cost still impeded their development and put hurdle for their industrial production. We develop a new type of triarylamine 3-hexylthiophene co-polymer (**TABT**) by using iron-catalyzed C–H/C–H polycondensation from simple C–H monomers. The obtained **TABT** polymers acted as high performance HTMs for methylammonium lead iodide-based perovskite (MAPbI₃) solar cells. The mesitylene substituted **TABT** (Mes-TABT) polymer exhibits perfectly matched ionization potential (IP = 5.4 eV) towards MAPbI₃, high hole-carrier mobility, and high-quality film coverage with uniform morphology, resulting optimal solar cell device of an enhanced power conversion efficiency (PCE) of 21.3% with an open circuit voltage of 1.15 V and device stability over 1000 hours, which are all superior than control devices made of state-of-the-art polymer HTM, poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (**PTAA**).

Part 2. Iron-catalyzed Tandem Cyclization of Diarylacetylene to a Strained 1,4-Dihydropentalene Framework for Narrow-band-gap Materials

Chen, M.; Sato, W.; Shang, R.*; Nakamura, E.* *J. Am. Chem. Soc.* **2021**, *143*, 6823–6828

Carbon-bridged *p*-arylenevinylenes present an emerging class of π -conjugated semiconductive materials of high stability and high responsiveness to external stimuli, which have found various applications in organic electronics. The carbon bridges flatten the system to tune electronic coupling between arylene and vinylene moieties and contribute significantly to the chemical stability by suppressing intermolecular interaction. However, not as carbon-bridged arylene systems, where synthetic installation of carbon bridge by Friedel-Crafts reaction is generally competent without undesired side reactions, a cation mechanism for installation of carbon bridges

between arylene and vinylene is less effective because of the susceptibility of vinylene moiety towards cationic rearrangement. Synthetic method developed for synthesis of carbon-bridged *p*-phenylenevinylene by accessing 3-lithioindene intermediate followed by Friedel-Crafts reaction suffers from undesired cationic rearrangement and limited synthetic scope for arylene units other than phenylene.



In this work, we have developed an iron-catalyzed tandem cyclization of a diarylacetylene to a strained 1,4-dihydropentalene framework incorporated in carbon-bridged arylenevinylene. The modular four-step synthesis eliminates the problematic carbolithiation and carbenium rearrangement encountered in the previous synthesis, and provides an expeditious access to a class of fused thiophene molecule **CTV**, that have a high HOMO level and a narrow HOMO–LUMO gap. **CTV** acts as an effective donor moiety in NFA materials to absorb near IR light above 1000 nm in a film state, and enables fabrication of a NIR organic photodetector device that shows an EQE value of 72.4% at 940 nm. With the facile synthetic access using iron catalysis, we expect that **CPVs** and **CTVs** will find a broad use in design and development of small molecules and polymeric optoelectronic materials

5. 主な発表論文等

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3. 雑誌名 Chemistry of Materials	6. 最初と最後の頁 5337 ~ 5344
掲載論文のDOI (デジタルオブジェクト識別子) 10.1021/acs.chemmater.1c01441	査読の有無 有
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〔図書〕 計0件

〔出願〕 計5件

産業財産権の名称 光電変換素子及び太陽電池モジュール	発明者 中村 栄一, SHANG Rui, et al.	権利者 同左
産業財産権の種類、番号 特許、特開2019-46935	出願年 2019年	国内・外国の別 国内

産業財産権の名称 新規鉄触媒を用いた共役高分子合成方法	発明者 中村 栄一, SHANG Rui, 佐藤 済, 道場 貴大	権利者 同左
産業財産権の種類、番号 特許、特願: 2020-130678	出願年 2020年	国内・外国の別 国内

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産業財産権の種類、番号 特許、特願: 2020-130217	出願年 2020年	国内・外国の別 国内

産業財産権の名称 量子ドット及びその作製方法	発明者 中村 栄一, SHANG Rui et al	権利者 同左
産業財産権の種類、番号 特許、特願: 2020-156302	出願年 2020年	国内・外国の別 国内

産業財産権の名称 光電変換素子及び太陽電池モジュール	発明者 中村 栄一, Shang Rui, 周 忠敏, 武井 出	権利者 同左
産業財産権の種類、番号 特許、特開2020-13898	出願年 2019年	国内・外国の別 国内

〔取得〕 計0件

〔その他〕

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6. 研究組織	氏名 (ローマ字氏名) (研究者番号)	所属研究機関・部局・職 (機関番号)	備考
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7. 科研費を使用して開催した国際研究集会

〔国際研究集会〕 計0件

8 . 本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関
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