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研究課題名(和文) Irradiation-Responsive Ligands for Efficient Iron-Catalysis

研究課題名(英文) Irradiation-Responsive Ligands for Efficient Iron-Catalysis

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研究成果の概要(和文)：本研究はベンゼンなど炭化水素の構成要素であり安定な炭素-水素結合を均一系鉄触媒によって、温和な条件下、一段階で炭素-炭素結合に変換する手法を開発した。持続可能な開発目標の観点から「ありふれた元素」を用いた有機合成触媒の開発が望まれており、地球上に大量に存在する鉄の触媒作用に関する重要な発見である。本反応によれば二種類のことなる芳香族化合物のクロスカップリングにおいて、100%の選択率で有機エレクトロニクス材料の簡便、安価、低毒性の合成が可能である。本成果は環境負荷の高い金属触媒に頼る化学反応から脱却し、有用な有機化合物を効率よく提供することで人類の持続的発展を可能にすることが期待される。

研究成果の学術的意義や社会的意義

そこで今回我々は、鉄の触媒作用に着目し、等量の基質の存在下、両基質の炭素-水素結合を切断し、効率的に炭素-炭素結合を生成する反応の開発に成功した。本成果は恒星内元素合成により宇宙に普遍的に存在する鉄を触媒として用い、自然界に豊富に存在する有機化合物から少工程数・低コストで有用な有機化合物を合成するという究極的な目標達成の先駆けであり、環境負荷の高い金属触媒に頼る化学反応から脱却し、有用な有機化合物を提供することで人類の持続的発展を可能にすることが期待される。

研究成果の概要(英文)：In this study, we developed a Fe-catalyzed method to convert stable arene C-H bonds, which are ubiquitous components of organic molecules, into carbon-carbon bonds in one step under mild conditions with high selectivity. From the viewpoint of sustainability, catalysts for organic synthesis using "ubiquitous elements" is desired, and it is most desirable to develop synthetic methods that use iron, which is the most abundant metal in earth. In this research, a simple, inexpensive, low toxic Fe-catalyzed synthetic method was developed to selectively cross-couple two arene C-H bonds with 100% selectivity. The high selectivity allows facile synthesis of organic electronic materials in a low cost and straightforward manner. This result provide a new way to synthesize valuable molecules of materials interest without using expensive and toxic metal catalyst that raising sustainability and environment issues, and will be beneficial for the future sustainable development of human society.

研究分野：有機化学

キーワード：鉄触媒 炭素-水素活性化 炭素-炭素結合 選択率 有機エレクトロニクス材料

様式 C-19、F-19-1、Z-19、CK-19 (共通)

1. 研究開始当初の背景

Based on recent developments and mechanistic understandings of iron-catalyzed direct C-H functionalization, we realized that ligand possessing a conjugated backbone is effective to tune the spin state of iron catalyst to cleavage C-H bond through a spin acceleration pathway. We hypothesized that by developing a new iron based catalytic system employing conjugated irradiation responsive ligands to use visible light irradiation will allow to achieve novel iron-catalyzed C-H activation/cross couplings with broad substrate scope and high selectivity.

2. 研究の目的

The purpose of the present research is the development of new irradiation-responsive ligands that are able to tune the spin state of iron-catalyst for the further development of efficient iron-catalysis. I will focus on synthesizing irradiation-responsive ligand having irradiation-responsive backbone structures, such as BDP (benzodipyrrole), BDT (benzodithiophene), and COPVs (carbon-bridged oligo(phenylenevinylene)s, and then study the optical properties of these new ligands and their iron complexes. These new ligands and their iron-complexes will be further utilized to develop challenging iron-catalyzed C-H functionalization under suitable irradiation conditions.

3. 研究の方法

In order to test the effect of irradiation-responsive ligand in iron-catalyzed C-H activation, we tried to make several types of ligands we proposed. Including bisphosphine ligand, triphosphine ligand, and dinitrogen ligand possessing several different types of conjugated backbones, such as benzodipyrrole or carbon-bridged phenylene vinylene structure. We tested various types of arene substrates of interest in materials science, such as conjugated thiophene derivatives, as substrates in iron-catalyzed C-H activation reactions. We also tried to develop new catalyst and ligand system to achieve iron-catalyzed two fold C-H activation/cross couplings with broad substrate scope and high selectivity.

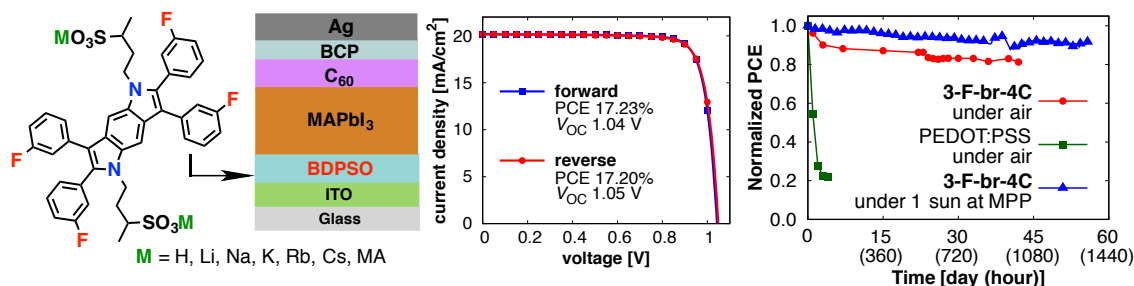
4. 研究成果

(1) Developed new hybrid type hole-transporting materials for achieving high performance perovskite solar cell of improved stability.

Shang, R.*; Zhou, Z.-M.; Nishioka, H.; Halim, H.; Furukawa, S.; Takei, I.; Ninomiya, N.; Nakamura, E*. *J. Am. Chem. Soc.* **2018**, *140*, 5018.

We synthesized a series of conjugated benzodipyrrole derivatives with the expectation to develop new conjugated irradiation-responsive ligand for iron catalysis. During the investigation of the photophysical and electrochemical properties of benzodipyrrole compounds, we realized that this type of molecules can be applied as promising materials in perovskite solar cells to transport photo-generated holes. We developed this kind of molecules into a new kind of hybrid type hole-transporting materials for solar cells. Our research achievement on this topic is briefly summarized below:

Hole-transporting material (HTM) is an indispensable constituent in organic electronic devices, generally comprising a donor/dopant combination, where the dopant often adversely affects other functional layers. We reported that substituted benzo[1,2-*b*:4,5-*b'*]dipyrrole bearing two racemic alkanediylsulfonate anion side chains (BDPSOs) serves as a neutral dopant-free HTM for lead perovskite (PV or MAPbI₃) solar cells. This ionic small molecule has a number of desirable properties such as a tunable HOMO/LUMO level, controllable solubility in different solvents, and non-hygroscopicity. A fluorinated disodium BDPSO shows good energy level matching with MAPbI₃, affording an inverted-structure solar cell that performs with 17.2% efficiency and with little hysteresis. The device without encapsulation exposed to ambient air retains >80% of its initial PCE value after storage for 40 days, and an encapsulated device retained >90% of its initial PCE after 1300 h at maximum power point under continuous light soaking. The counter cation in hybrid BDPSO materials is exchangeable to allow facile preparation of a series of dialkylmetal BDPSOs (H, Li, Na, K, Rb, Cs, MA). Performance and stability of PV solar cells using BDPSOs can be further improved by modifying the component of counter cations in BDPSOs. The origin of the observed effect of BDPSOs to stabilize PV device and to remove hysteresis is rationalized by its hybrid ionic nature to passivate defects at interface and grain boundaries.



(2) Highly Selective Iron(III)-Catalyzed Two-fold C(sp²)-H Activation/C-C Cross-Coupling of Heteroarene with Carboxamide using a Transient Substrate Connection Strategy
 Doba, T.; Matsubara, T.; Ilies, L.; **Shang, R.***; Nakamura, E.* *Nat. Catal.* **2019**, *2*, 400.

During the investigation of using irradiation-responsive ligand for iron-catalyzed C-H activation of thiophene derivatives, we discovered a new type of transient connection strategy to achieve iron-catalyzed twofold C-H activation/cross coupling with absolutely cross coupling selectivity. The method is applicable to the functionalization of photo-responsive conjugated thiophene molecules of interest in materials science. The research achievement on this topic is summarized below in detail:

Cross-coupling reaction through twofold C-H activation on both coupling partners without pre-functionalization is the ideal transformation to forge C-C bond regarding to step-efficiency and atom economy. However, selectivity issue is always a problem in such reactions because two C-H bonds much be activated sequentially with desired selectivity to prevent undesired homo-couplings. We conceived that, iron(III) catalyst which has its distinct way to cleave arene C-H bonds compared with late transition-metal catalyst, may be promising to address this issue. Iron catalyst for C-H activation has been well accepted for its sustainability, low cost, and low toxicity. However, though have been actively explored in the past decades, iron-catalyzed C-H activation reactions are still limited in the frames of coupling C-H bonds with pre-functionalized organometallic reagents or electrophiles (Figure 1, a). For achieving iron-catalyzed twofold C-H activation/cross-coupling, second C-H activation step on a ferracycle intermediate is necessary, while a ferracycle intermediate activates arene C-H bond to access a diaryliron species is rarely reported in literature (Figure 1, b). With the recent mechanistic understanding that an organoiron(III) species selectively activate C-H bonds via *s*-bond metathesis to form a putative hexa-coordinated ferracycle (III) intermediate (Figure 1, c), we hypothesized the formed iron(III) metallocycle can undergo second C-H bond activation with an arene substrate to generate a diaryliron(III) intermediate. Diaryliron(III) intermediate further undergoes reductive elimination to produce biaryl product and iron(I), which can be turned to iron(III) using dichloroalkane as oxidant. Thus, an Fe(III)/Fe(I) catalytic cycle fits the mechanistic requirement for two fold C-H activation/cross-coupling using iron(III) precatalyst. Herein, we report that a combination of iron(III) salt with bisphosphine ligand effectively catalyzes twofold C-H activation/cross-coupling of heteroarene with hetero(arene) carboxamide in the presence of an organozinc reagent as base and a dichloroalkane reagent as oxidant. The detailed example is demonstrated in Figure 1, d. A THF solution of ((trimethylsilyl)methyl)magnesium chloride (5.4 equiv.) was added to a THF solution of 3-methyl-N-(quinolin-8-yl)benzamide (0.40 mmol, 1.0 equiv.) and zinc chloride (0.88 mmol, 2.2 equiv.) to deprotonate the amide proton and generate 2.2 equiv of diorganozinc base. Then, benzo[*b*]thiophene (0.40 mmol, 1.0 equiv.), 1,2-dichloropropane (DCP, 2.0 equiv.) and a THF solution of Fe(acac)₃ (20 mol %) and *cis*-1,2-bis(diphenylphosphino)ethylene (dppe, 20 mol %) were sequentially added and the reaction mixture was stirred at 70 °C for 18 h. After aqueous work up, the C-H/C-H cross-coupled product **1** was obtained in 86% yield without detecting any homo-coupling product from benzothiophene (**2**) or from carboxamide (**3**). The reaction exclusively took place at the C2 position on thiophene ring, and no C3-functionalized benzothiophene product was detected. Carefully analyzing the side-product and mass balance of this reaction revealed that the major side product was a small amount (~ 5%) of alkylated arene carboxamide. Homo-coupling of ((trimethylsilyl)methyl)magnesium chloride and alkylated benzothiophene were not formed. Benzothiophene was recovered approximately in 15% yield, which accounts for the obtained 86% yield of **1**. Analyzing the mass balance and side product revealed no sign of pre-reduction of iron(III) species in the catalytic cycle, which was similarly observed in our previously reported organoiron(III) catalyzed C-H activation with aryl boronate reagents through *s*-bond metathesis. Using a slightly increased amount of 3-methyl-N-(quinolin-8-yl)benzamide (1.1 equiv.) resulted in forming arylated benzothiophen (**2**) in 90% yield, and further increase the amount of 3-methyl-N-(quinolin-8-yl)benzamide to 1.25 equivalent allowed full conversion of benzothiophene to

deliver **1** in 97% yield (25 mol % catalyst, 2.5 equiv of DCP).

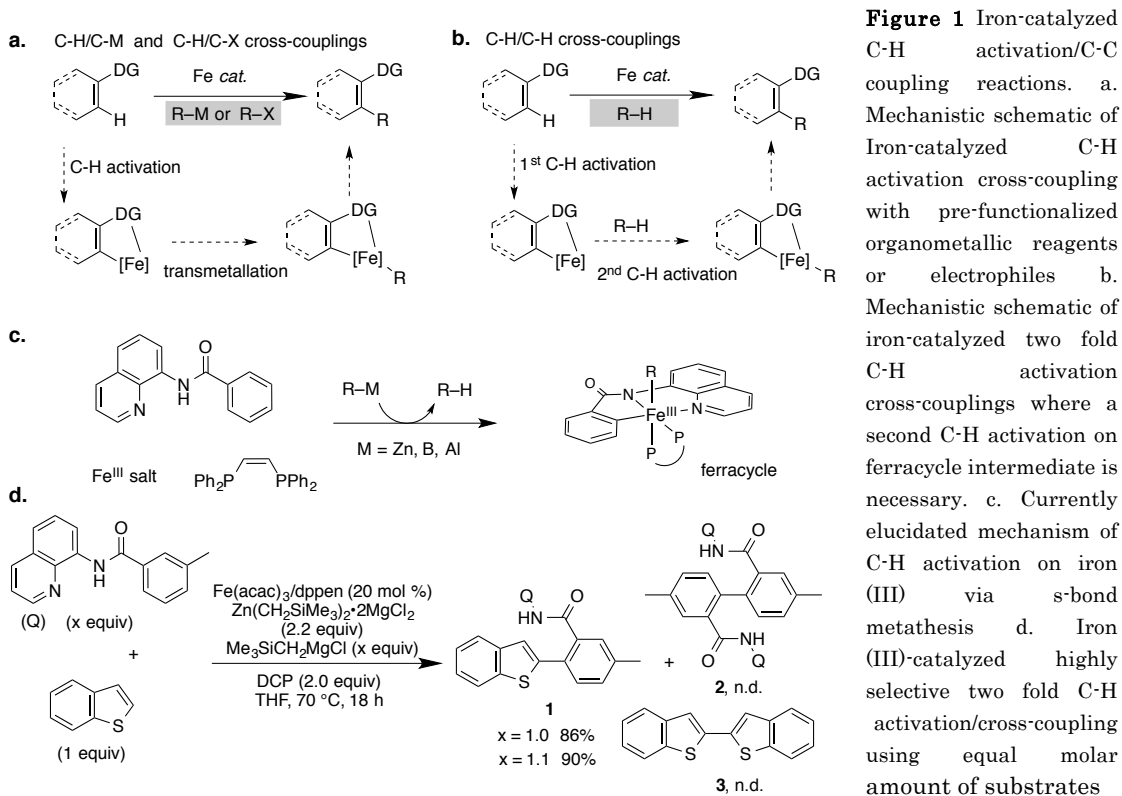
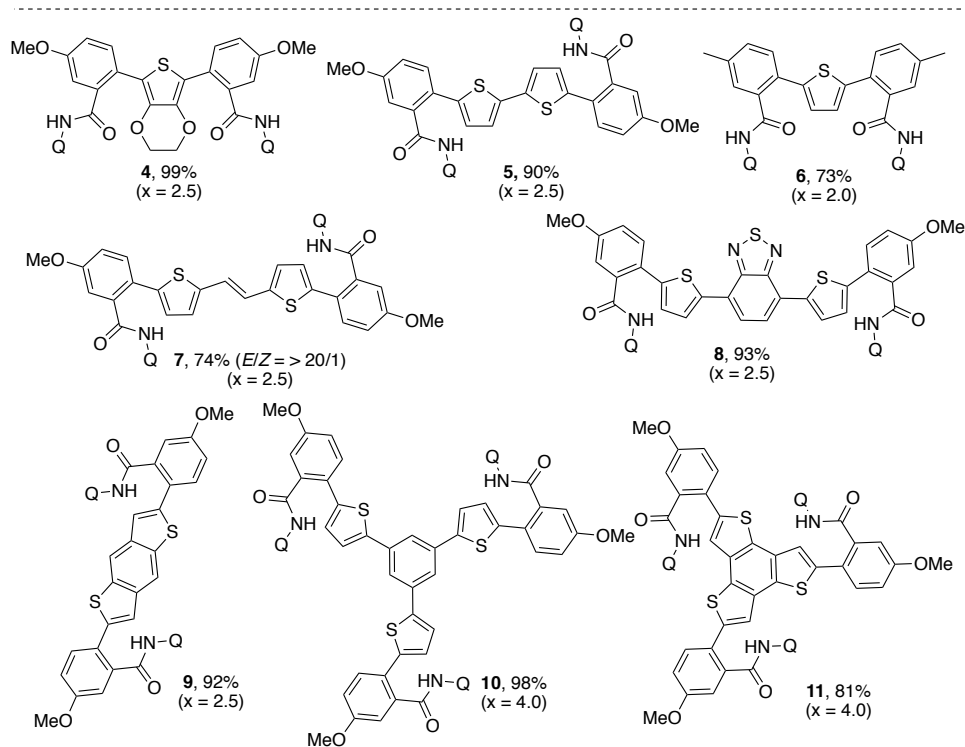


Figure 1 Iron-catalyzed C-H activation/C-C coupling reactions. a. Mechanistic schematic of iron-catalyzed C-H activation cross-coupling with pre-functionalized organometallic reagents or electrophiles b. Mechanistic schematic of iron-catalyzed two fold C-H activation cross-couplings where a second C-H activation on ferracycle intermediate is necessary. c. Currently elucidated mechanism of C-H activation on iron (III) via s-bond metathesis d. Iron (III)-catalyzed highly selective two fold C-H activation/cross-coupling using equal molar amount of substrates



Scheme 1 Iron-catalyzed C-H activation/C-C coupling using thiophene derivatives of materials interest

The remarkable feature of this iron-catalyzed C-H/C-H cross-coupling is its overwhelmingly high selectivity of cross-coupling without any homo-coupling detected. Distinct from literature examples of C-H/C-H coupling of carboxamide and thiophene derivatives catalyzed by other transition-metal catalysts, where thiophene derivatives were always used in excess, our reaction allows the use of thiophene derivatives as limiting reagent to achieve high yield. The high chemo-selectivity of cross-coupling and regio-selectivity of arylation only at C2 position encouraged us to further test our method on various conjugated thiophene molecules. The directing group is expected to further convert to a carbon bridge in pi-conjugated molecules to extend flat pi-conjugation. As depicted in Scheme 1, 3,4-ethylenedioxythiophene, a electron-rich thiophene unit used in conductive polymer and

hole-transporting materials is successful di-arylated at 1, 4-position in quantitative yield with only 2.5 equivalent amount of carboxamide used (**4**). Since electron-rich thiophene is easy to be oxidatively oligomerized in the presence of oxidant, it is a challenge substrate and seldomly demonstrated in C-H/C-H oxidative coupling reactions. The successful application of 3,4-ethylenedioxythiophene demonstrated the synthetic advantage of iron-catalyzed reaction system which applies a very mild oxidant not detrimental to large pi-conjugated electron-rich system. 2,2'-Bithiophene was diarylated at 5- and 5'-position in 90% yield without detecting any regioisomer (**5**). Remarkably, thiophene can be smoothly 2,5-diarylated in 73% yield with 16% of monoarylation using only 2.0 equivalent of benzamide substrate, demonstrating the high reaction efficiency (**6**). (E)-1,2-di(thiophen-2-yl)ethane was diarylated without isomerizing the double bond (**7**). 4,7-Di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole, a thiophene structure found in organic photovoltaic materials containing an middle electron accepting unit, underwent smooth diarylation in 93% yield (**8**). p-Extended benzo[1,2-*b*:4,5-*b'*]dithiophene was amenable to be diarylated at C2 and C6 position in excellent yield (**9**). Beside diarylation, triarylation took place efficiently with 1,3,5-tri(thiophen-2-yl)benzene benzo[1,2-*b*:3,4-*b'*:5,6-*b''*]trithiophene (**10**, **11**). Admittedly, although reaction efficiencies are high with low substrate ratio, the catalyst loadings for the di- and tri- arylation of thiophene are high (20 -25 mol% for each C-H/C-H bond formation). However, the dppe ligand can be recovered in 89% yield after the reaction without stereo-isomerization.

5. 主な発表論文等

〔雑誌論文〕 (計 2 件)

(1) Disodium Benzodipyrrole Sulfonate as Neutral Hole-Transporting Materials for Perovskite Solar Cells, R. Shang,* Z. Zhou, H. Nishioka, H. Halim, S. Furukawa, I. Takei, N. Ninomiya, E. Nakamura,* [*J. Am. Chem. Soc.*, **140**, 5018-5022 \(2018\)](#).

(2) Homocoupling-free Iron-catalysed Twofold C-H Activation/Cross-couplings of Aromatics via Transient Connection of Reactants, T. Doba, T. Matsubara, L. Ilies, R. Shang,* E. Nakamura,* [*Nat. Catal.*, **2**, 400-406 \(2019\)](#).

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(1) 発表者名: Rui Shang, Zhongmin Zhou, Hiroki Nishioka, Eiichi Nakamura 発表標題: Benzo[1,2-*b*:4,5-*b'*]dipyrrole Sulfonate Salts as Neutral Dopant-Free Hole-transporting Materials for Highly Efficient and Stable Perovskite Solar Cells 学会等名: International Symposium on Supramolecular Chemistry & Functional Materials 2018 (CEMSupra 2018) 発表年: 2018

(2) 発表者名: Ziyue Qiang, Henry Halim, Rui Shang, Eiichi Nakamura 発表標題: Glycine-HCl Modulated Growth of Oriented Lead Perovskite Crystals for Efficient Solar Cells 学会等名: The 98th CSJ Annual Meeting 発表年: 2018

(3) 発表者名: Rui Shang, Zhongmin Zhou, Hiroki Nishioka, Henry Halim, Shunsuke Furukawa, and Eiichi Nakamura 発表標題: Disodium Benzodipyrrole Sulfonate as Neutral Dopant-Free Hole-transporting Materials for Perovskite Solar Cells 学会等名: The 98th CSJ Annual Meeting 発表年: 2018

(4) 発表者名: Rui Shang, Zhongmin Zhou, Hiroki Nishioka, Eiichi Nakamura 発表標題: Benzo[1,2-*b*:4,5-*b'*]dipyrrole Sulfonate Salts as Neutral Dopant-Free Hole-transporting Materials for Highly Efficient and Stable Perovskite Solar Cells 学会等名: International Symposium on Energy Science and Technology 2018, OIST, Okinawa, 発表年: 2018 年

(5) 発表者名: Rui Shang. 発表標題: Irradiation-excited Palladium-catalysis through Blending Radical and Organometallic Reactivity. 学会等名: Beilstein Organic Chemistry Symposium 2018:Photoredox Catalysis for Novel Organic Reactions. 発表年: 2018 年

(6) 発表者名: Rui Shang 発表標題: Benzodipyrrole Sulfonate Salts as Neutral Dopant-Free Hole-transporting Materials for Perovskite Solar Cells. 学会等名: The China-Japan Workshop for Innovations in Molecular Science and Technology. 発表年: 2018 年

(7) 発表者名: Rui Shang, Zhongmin Zhou, Hiroki Nishioka, Henry Halim, Shunsuke Furukawa, and Eiichi Nakamura 発表標題: Hybrid Benzodipyrrole Sulfonate Salt Materials in Perovskite Solar Cell Application 学会等名: The 29th Japan Symposium on Physical Organic Chemistry 発表年: 2018 年

(8) 発表者名: Rui Shang and Eiichi Nakamura 発表標題: Hybrid Benzodipyrrole Sulfonate Salt Materials in Perovskite Solar Cell Applications 学会等名: The 14th International Kyoto Conference on New Aspects of Organic Chemistry (IKCOC-14) 発表年: 2018 年

(9)発表者名: Rui Shang and Eiichi Nakamura 発表標題: Synthetic Development of Organic Materials for Perovskite Solar Cell Applications 学会等名: The 99th CSJ Annual Meeting 発表年: 2019 年

〔図書〕(計 0 件)

〔産業財産権〕

○出願状況(計 1 件)

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, ルイ シャン (Rui Shang), ツオンミン ツォウ, 武井出

権利者: 同上

種類: 特許

番号: 特願 2017-167613 号

出願年: 平成 30 年

国内外の別: 国内

6. 研究組織

(1)研究分担者

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所属研究機関名:

部局名:

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研究者番号(8桁):

(2)研究協力者

研究協力者氏名: なし

ローマ字氏名:

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