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研究課題名(和文) Exploration of facile synthesis for functional porphyrinoids and investigation of their applications

研究課題名(英文) Exploration of facile synthesis for functional porphyrinoids and investigation of their applications

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研究成果の概要(和文)：我々が合成に成功したNiNCは、従来の反芳香族化合物とは異なった高い安定性を示す興味深い化合物である。今回、NiNCを用いて反芳香族化合物を積層させると芳香族性が発現することを世界で初めて実証した。様々な機能性化合物の合成にも成功し、その成果を報告した。具体的にはbodipyとヘキサフィリンのハイブリッド化合物を用いたアンテナシステムや、反芳香族性NiNCを電極として用いた有機リチウム電池及び全有機化合物電池の開発にも取り組んだ。その結果、高い安定性や優れた電池性能を達成し、新たな有機電池としての可能性を示した。

研究成果の概要(英文)：Nickel(II) norcorrole (NiNC) which exhibits characteristic antiaromatic properties and a reasonable chemical-stability has been synthesised in our research group, and further investigated to study its interesting magnetic features created by molecular stacking. The molecular stacking induces aromaticity on antiaromatic molecules was experimentally proved.

NiNC was also applied for an active electrode material of Li-organic and Li-free organic batteries. The batteries performed remarkably charge/discharge processes over 100 cycles and showed high discharge capacity with great efficiencies.

Furthermore, various functional porphyrinoids and their hybrid molecules were synthesized through our research, and interesting properties of the molecule and application approaches were reported through conferences and research papers. Some of the publications were highly cited, selected as hot papers, and invited to the journal frontispieces.

研究分野：有機化学

キーワード：構造有機化学

1. 研究開始当初の背景

- ① Expanded porphyrins comprising large π -conjugation pathways have shown enhanced optical, electrochemical, and coordination properties. Their usefulness in various practical applications has led to a flurry of research activity on their structures, synthetic methods, and representative chemical/physical properties.
- ② In 2001, applicant and prof. Osuka have reported a facile synthesis of a series of *meso*-aryl substituted expanded porphyrins, including an acid-catalyzed condensation of pentafluorobenzaldehyde and simple pyrrole (*JACS* **2001**, 12, 7190; *ACIE* **2001**, 40, 619). Since their distinct physical/electrochemical properties have been exceedingly studied (*TL* **2003**, 44, 2505; *ACIE* **2003**, 42, 78; *EJOC* **2008**, 1341; *CEJ* **2009**, 12955), and some molecules have been reported as powerful suppliers of specific magnetism (*JACS* **2008**, 130, 1824), investigation of the novel types of functional expanded porphyrins has been the aim of the applicant's research.
- ③ The applicant has reported a facile synthetic method of Ni(II) norcorrole, 'metal-templated intramolecular coupling' (*ACIE* **2012**, 51, 8542, The article has been selected for a highlight in *SAYNFACTS*). Also, the applicant found that the 32π -electron containing *meso*-aryl substituted Ni(II)₂ octaphyrin(1.0.1.0.1.0.1.0) is isolable. Accordingly, the metal-templated intermolecular coupling is a challengeable synthetic method to produce octaphyrin(1.0.1.0.1.0.1.0) and it is probably the appropriate method to improve the synthetic yield. The reasonably stable antiaromatic character of the octaphyrin is also quite attractive. In principle, Pd(II) ion forms a square-planar complex where the consequent C-C coupling to complete its cyclic structure from the initial C-C bond formation occurs within a longer distance. Consequently, Pd(II) dipyrin complex can form a dimeric structure which forces an intermolecular coupling to get a larger macrocycle having eight pyrrole units. Our preliminary research has proved the selective formation of Pd(II) octaphyrin(1.0.1.0.1.0.1.0) from the Pd(II) precursor (*ACIE* **2013**, 52, 13727).
- ④ Interruption of heteroatoms in the main skeleton of porphyrin analogues creates useful functions. Also, investigation of the reactivity of the heteroatom-containing porphyrinoids is an attractive research topic related to the formation of enhanced functional materials. In early stage, we found that treatment of 5,15-diazoporphyrin with alkyl lithium in toluene at

low temperature regioselectively provides monoalkylated diazachlorins. Interestingly, the resulting products exhibited bathochromically shifted and intensively enhanced Q-band (*Chem. Commun.* **2003**, 49, 5046).

- ⑤ Antiaromatic porphyrinoids exhibiting intriguing properties such as small HOMO-LUMO gaps and high redox activity would be manipulated for practical applications. However, most antiaromatic compounds are unstable or difficult to prepare in large quantity for use in practical applications. Since a facile and large-scale synthesis of antiaromatic, dimesityl-substituted norcorrole Ni(II) (NiNC) has been accomplished with over 90% yield. The applicant applied the antiaromatic NiNC to electrode-active materials in rechargeable batteries. The Li-NiNC and Li-free NiNC batteries well performed their charge/discharge processes enough to prospective battery materials. On the basis of the results, the antiaromatic expanded porphyrins are also applicable in high performance batteries as the electrode-active materials.

2. 研究の目的

This research aimed to establish practical synthesis of functional porphyrin analogues. Porphyrinoids have interesting properties such as multi-redox and unique coordination behavior, but the synthesis of them is not effective. In the early research, the applicant has found the formation of an expanded porphyrin by metal-template strategy. Based on this finding, the applicant challenged to synthesize expanded porphyrins efficiently.

Investigation of their structure, properties, and functions was another goal of this research with the approaches in practical applications.

3. 研究の方法

In the research, the applicant focused on ① **establishing facile synthetic procedures for expanded porphyrins by using dipyrin metal complexes.** ② **Synthesis of hetero-atom-containing porphyrin analogues** was another goal. Investigation of the sequential procedures for functional porphyrin analogues was tried to stimulate ③ **the study of their significant chemical/physical properties. The artificial compounds were approached for practical applications.**

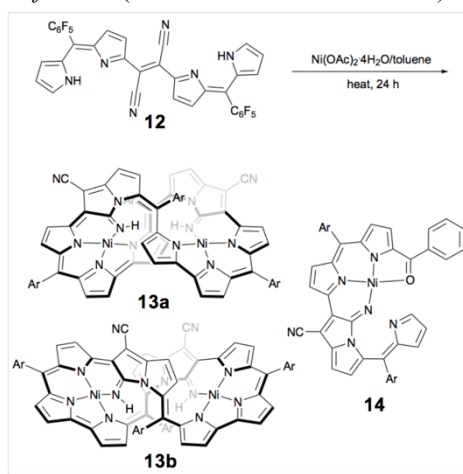
4. 研究成果

We succeeded in investigations of new functional porphyrin analogues having interesting molecular properties and approaches for their practical

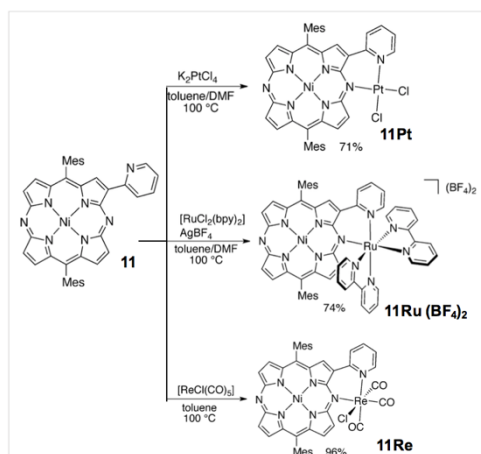
applications.

<Synthetic approaches towards functional porphyrin analogues>

① **Investigation of synthetic method of bisNi^{II} expanded porphyrinoid complexes:** It was found that Ni^{II}-metallation of dicyanovinylene-bis(*meso*-aryl)dipyrrin **12** under refluxed toluene conditions resulted in the formation of a bicyclic pyrrolizine ring to afford two isomeric bisNi^{II} expanded porphyrinoid complexes **13a** and **13b**. Furthermore, acyclic Ni^{II} dipyrrin complex **14** was also isolated. The respective structures for **13a**, **13b**, and **14** were elucidated by X-ray diffraction analysis. Macrocycles **13a** and **13b** exhibited typical features of aromatic porphyrinoids showing their longest wavelength absorption bands in the near infrared region from 1100 to 1600 nm. The result was reported through *CSJ conference* (日本化学会第 97 春季年会).

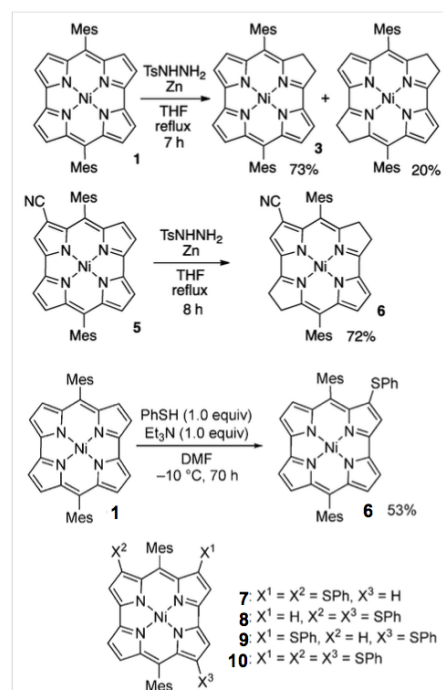


② **Investigation of hetero-atom-containing functional porphyrin analogues:** A metal porphyrinoid containing a hetero-atom (nitrogen), nickel(II) 3-pyridyl-5,15-diazaporphyrin was used as a bidentate metalloligand platform for platinum(II), ruthenium(II), and rhenium(I) cations which provided great chemical properties. Single

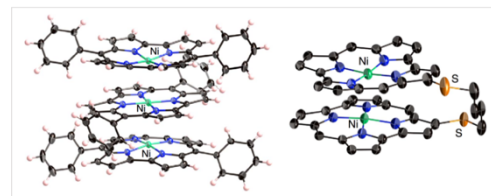


crystal structures showed the presence of a dative bond between the outer metal center and the *meso*-nitrogen atom and due to the outer-metal coordination, the UV/Vis absorption bands were substantially red-shifted (*ACEI 2014*, 53, 13924).

③ **Investigation of functional NiNC family molecules:** Introduction of phenylthio groups to NiNC dramatically decreased HOMO-LUMO gap of the norcorrole unit and enhanced its optical property near IR range (*ACEI 2015*, 54, 8454). Reactivity of NiNC was also investigated to provide reduced forms of NiNC (*CC 2016*, 52, 7104).



④ **Investigation of functional NiNC molecules and their attractive magnetic properties:** Antiaromatic NiNC molecules exhibiting both characteristic antiaromatic behaviors and reasonable stability have been investigated to produce new magnetic features by molecular stackings: the molecular stacking that has been induced by bridging groups sequentially created aromaticity on antiaromatic molecules. This marvelous system was published in *Nature Communications* (2016, 13620).



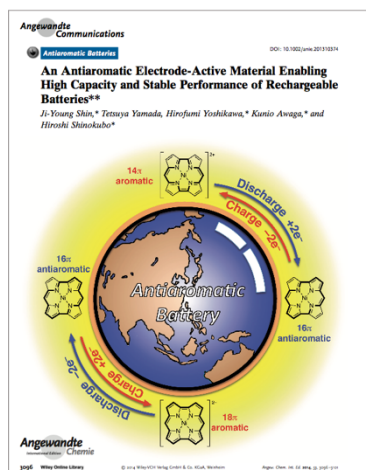
Antiaromatic NiNC was treated with a kinetically stabilized silylene, which gave ring-expansion products in excellent yields. The reaction happened through highly regio- and stereoselective insertions was investigated on NiNC and the results were published in

Angewandte Chemie (*ACIE*. 2014, 53, 1506, frontispiece)

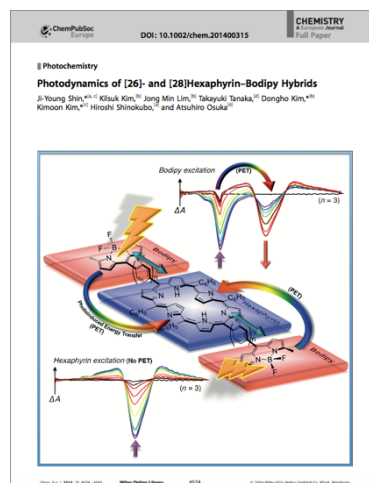


<Approches for practical applications>

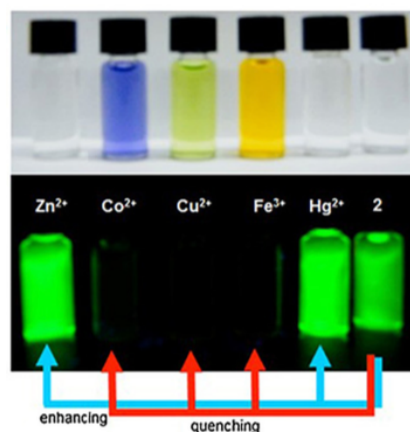
① **Use as an active electrode material in artificial batteries:** Antiaromatic NiNC was applied to an active electrode for Li-organic and Li-free organic batteries. Those batteries remarkably performed charge/discharge processes in high discharge capacities (207 mAhg⁻¹ over 100 cycles for the Li-NiNC battery and about 200 mAhg⁻¹ over 100 for the NiNC-NiNC battery) and showed great efficiencies. These results were reported and highlighted in Angewandte Chemie (*ACIE* 2014, 53, 3096, hot paper & frontispiece).



② **Approach towards antenna system (photochemical study):** To examine photoinduced energy transfer (PET) process from bodipy (energy donor) to hexaphyrins (26 and 28 π-electrons pathways, energy acceptors), a set of hybrids having gradual variations in the distance between hexaphyrin and bodipy segments were synthesized. The PET processes associating with their center-to-center distances were observed efficiently in the hybrids, without any other disruption (*Chem. Eur. J.* 2014, 20, 4574, frontispiece).



③ **Application as a chemosensor:** Chemosensing behaviors (either quenching or enhancing its fluorescence origin) of ethynyl bodipy having pyridyl terminal units toward various transition metal ions were investigated. A large fluorescence enhancement was observed upon treatment of Zn²⁺ whereas additions of Fe³⁺, Co²⁺, and Cu²⁺ caused fluorescence quenching. This behavior would be capable for its potential application as a turn-on fluorescent chemosensor for Zn²⁺.



5. 主な発表論文等

〔雑誌論文〕 (計 11 件)

- ① Ryo Nozawa, Hiroko Tanaka, Won-Young Cha, Yonseok Hong, Ichiro Hisaki, Soji Shimizu, Ji-Young Shin, Tim Kowalczyk, Stephan Irle, Dongho Kim, Hiroshi Shinokubo, Staked antiaromatic porphyrins, *Nature Commun.*, 査読有, 2016, 13620, doi:10.1038/ncomms13620
- ② Ryo Nozawa, Keitaro Yamamoto, Ichiro Hisaki, Ji-Young Shin, Hiroshi Shinokubo, Ni(II) tetrahydronocorroles: antiaromatic porphyrinoids with saturated pyrrole units, *Chem. Commun.*, 査読有, 2016, 52, pp 7106-7109, doi:10.1039/C6CC02918C
- ③ Indranil Roy, Ji-Young Shin, Dinesh Shetty, Jayshree K. Khedkar, Jun Heuk Park, Kimoon

- Kim, E-Bodipy fluorescent chemosensor for Zn²⁺ ion, *J. Photochem & Photobio A-Chem.*, 査読有, 2016, 331, pp 233-239, <https://doi.org/10.1016/j.jphotochem.2015.08.015>
- ④ Ryo Nozawa, Keitaro Yamamoto, Ji-Young Shin, Satoru Hiroto, Hiroshi Shinokubo, Regioselective Nucleophilic Functionalization of Antiaromatic Nickel(II) Norcorrole, *Angew. Chem. Int. Ed.*, 査読有, 2015, 54, pp8454-8457. doi:10.1002/anie.201502666
- ⑤ Ji-Young Shin, Satoru Hiroto, Hiroshi Shinokubo, Macrocyclic dipyrin dimer bridged by ethylene and dioxyphenylene linkers, *J. Porphyrins & Phthalocyanines*, 査読有, 2015, 19, pp135-139. <http://dx.doi.org/10.1142/S108842461450093X>
- ⑥ Ayaka Yamaji, Ji-Young Shin, Yoshihiro Miyake, Hiroshi Shinokubo, 3-Pyridyl-5,15-diazaporphyrin nickel(II) complex as a bidentate metalloligand for transition metals, *Angew. Chem. Int. Ed.*, 査読有, 2014, 53, pp13924-13927. doi:10.1002/anie.201408852
- ⑦ Naruhiko Watch, Takeshi Kondo, Satoru Ito, Ji-Young Shin, Hiroshi Shinokubo, Synthesis, reactivity and property of 5,15-dithiaporphyrin copper(II) complex; *J. Porphyrins & Phthalocyanines*, 査読有, 2014, 18, pp 675-678. <http://dx.doi.org/10.1142/S1088424614500412>
- ⑧ Seung Bae Son, Qing Miao, Ji-Young Shin, David Dolphin, Jae Ryang Hahn, Ring and volcano structures formed by a metal dipyrromethene complex, *Bul. Kor. Chem. Soc.*, 査読有, 2014, 35, pp1727-1731. <https://doi.org/10.5012/bkcs.2014.35.6.1727>
- ⑨ Ji-Young Shin, Kilsuk Kim, Jong Min Lim, Takayuki Tanaka, Dongho Kim, Kimoon Kim, Hiroshi Shinokubo, Atsuhiko Osuka, Photodynamics of [26]- and [28]hexaphyrin-bodipy hybrids; *Chem. Eur. J.*, 査読有, 2014, 20, pp4574-4582. doi:10.1002/chem.201400315
- ⑩ Ji-Young Shin, Tetsuya Yanada, Hirofumi Yoshikawa, Kunio Awaga, Hiroshi Shinokubo, An antiaromatic electrode-active materials enabling high capacity and stable performance of rechargeable batteries, *Angew. Chem. Int. Ed.*, 査読有, 2014, 53, pp3096-3101. doi:10.1002/anie.201310374
- ⑪ Takaki Fukuoka, Kenya Uchida, Young Mo Sung, Ji-Young Shin, Shintaro Ishida, Jong Min Lim, Satoru Hiroto, Ko Furukawa, Dongho Kim, Takeaki Iwamoto, Hiroshi Shinokubo, Near-IR absorbing nickel(II) porphyrinoids prepared by regioselective insertion of silylenes into antiaromatic nickel(II) norcorrole; *Angew. Chem. Int. Ed.*, 査読有, 2014, 53, pp1506-1509. doi:10.1002/anie.201309921
- [学会発表] (計 5 件)
- ① Nathan H. Faialaga, Satoru Ito, Hiroto Shinokubo, Ji-Young Shin, A facile synthesis of novel expanded porphyrinoids: bisNi(II) complexes of dicyanovinylene-di(meso-aryl) dipyrromethene, 日本化学会第97春季年会, Keio University, Japan, Mar. 16~19, 2017.
- ② Ji-Young Shin, Tetsuya Yanada, Hirofumi Yoshikawa, Kunio Awaga, Hiroshi Shinokubo, Antiaromatic norcorrole batteries, Pacificchem2015, Honolulu, Hawaii, Dec. 15~20, 2015.
- ③ 野澤 遼、山本恵太郎、辛 知映、廣戸 聡、忍久保 洋、反芳香族ノルコロールニッケルの位置選択的な直接官能基化、日本化学会第95春季年会, Nihon University, Japan, Mar. 26~29, 2015.
- ④ 山本恵太郎、山口隆一、辛 知映、忍久保洋、反芳香族ノルコロールニッケル錯体の還元反応に関する研究、日本化学会第94春季年会, Nagoya University, Japan, Mar. 27~30, 2014.
- ⑤ 山路文香、辛 知映、三宅由寛、忍久保 洋、ピリジルジアザポルフィリンを二座配位子として有するレニウム錯体の合成と物性、日本化学会第94春季年会, Nagoya University, Japan, Mar. 27~30, 2014.
- [その他]
- 講演 (計 3 件)
- ① Ji-Young Shin, Dipyrin building block, The 52nd CMS international seminar, Kyushu University, Japan, Apr. 21, 2017, 招待講演.
- ② Ji-Young Shin, A study on organic batteries using porphyrinoid electrodes, preICMM 2016, Nagoya University, Japan, Sep. 2~3, 2016, 招待講演.
- ③ Ji-Young Shin, Tetsuya Yanada, Hirofumi Yoshikawa, Kunio Awaga, Hiroshi Shinokubo, Antiaromatic norcorrole batteries, IGER workshop on molecular electronics for young researchers, Nagoya University, Japan, Oct. 21-22, 2014.
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