

論文 / 著書情報
Article / Book Information

題目(和文)	光活性なヘキサアザフェナレン配位子からなるネットワークとその応用
Title(English)	Photoactive Hexaazaphenylene Ligand-based Frameworks and Their Applications
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

論文要旨

THESIS SUMMARY

系・コース： 化学 系
Department of Graduate major in 化学 コース
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Student's Name

申請学位 (専攻分野)： 博士 (理学)
Academic Degree Requested Doctor of
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要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words)

This thesis describes the investigation of photochemical processes of tri(4-pyridyl) hexaazaphenylene (TPHAP)-based molecules as a novel photosensitizer system by chemical and spectroscopic methods. The parent TPHAP and pyridinium-TPHAP derivatives were synthesized and characterized for their structural and physical properties. These molecules were used as photocatalysts, both as soluble species and as part of a solid-state scaffolds, to promote photooxidation reactions.

In **Chapter 1**, This chapter presents the background of thesis including the development of phenylene chemistry as a promising functional material in several applications, such as conductive materials, thermochromic devices, two-photon absorption and photocatalysts. Then, the methodology and application of pyridinium compound are summarized as general information for the modification of terminal pyridine of TPHAP molecule into pyridinium motif. Lastly, porous coordination networks (PCNs) incorporating photosensitizers as one of their components have the ability to generate ROSs upon light irradiation combined with the presence of accessible pores and other functionalities. However, the most commonly used ligands for the PCN construction do not possess the required light harvesting capabilities, which limits their utilization in photocatalytic transformations. Therefore, a series of materials based on the polycyclic hexaazaphenylene (HAP) anion, including pyridyl substituted analogue, TPHAP, pyridinium-TPHAP, as well as PCNs incorporating these molecules were studied in this thesis. The chief motivation for this study was the development of novel photocatalytic systems. The ROSs generation abilities and photostability of TPHAP derivatives were confirmed by spectroscopic analysis, selective oxidation reactions and X-ray diffraction analysis. Finally, the ability of these materials to oxidize a variety of substrates including the inert hydrocarbons through light irradiation was demonstrated.

In **Chapter 2**, The ROSs generation ability of TPHAP was successfully demonstrated by interrogating its homogeneous photocatalytic activity and spectroscopic characterization. The emission spectra originating from the intramolecular charge-transfer transition could be affected by exposure to the atmospheric air, which was ascribed to the energy and charge transfer from the excited state of TPHAP to oxygen molecules, producing ROSs. The dual nature of this process, which results in the formation of both radical and non-radical species, was additionally confirmed by the selective photocatalytic conversion of 1,5-dihydroxynaphthalene (1,5-DHN) and degradation of organic dye molecules. In particular, the kinetic parameters of 1,5-DHN photooxidation were determined from the time-dependent spectroscopic measurements. TPHAP was incorporated into a porous coordination network scaffold as a linker, in order to create a heterogeneous catalytic system and improve its utility for photocatalytic transformations. The resultant Cd(II) network, PCN 1, was successfully synthesized and was confirmed to retain the ROSs generation function of TPHAP. The photocatalytic activity of PCN 1 was tested for the alkane photooxidation reaction. The network catalyst displayed good photostability and catalytic efficiencies among pure coordination networks. Control experiments in the presence of several scavenger agents were performed, which revealed that the alkane photooxidation was facilitated by a number of ROSs generated through both energy and charge transfer processes from the excited state of PCN 1.

In **Chapter 3**, Pyridinium-TPHAP derivatives were obtained by N-alkylation reactions of TPHAP. The electronic structures of these compounds indicated the increase in intermolecular interactions was due to the changes in molecular charges, electronic states, and redox properties. Pyridinium modification was limited to the three terminal pyridine groups while the HAP core remained unreacted. The resultant molecules were isolated in their di-cationic states. In crystal structures, the presence of three cationic pyridinium groups and the anionic HAP core led to shortened π - π distances within the stacked HAP dimers. This effect was attributed to the decrease in anion-anion repulsion between the HAP cores. The steric hindrance from alkyl groups, as well as appearance of additional weak interactions from Van der Waals forces and weak hydrogen bonding directly affected the overall structural arrangement. In solution state,

the characteristic absorption bands of pyridinium analogues shifted to lower energy, whereas their reduction potentials occurred at less cathodic values. Moreover, the changes in the absorption spectra associated with the electrochemical reduction suggested that these compounds exhibited useful electrochromic properties. These results demonstrated the utility of the pyridine-to-pyridinium modification in enhancing the functionality of **TPHAP** and increasing the interactivity in its molecular packing.

In **Chapter 4**, the effect of the changes on electronic properties of the pyridinium-**TPHAP** system was tested by performing the 1,5-DHN photooxidation reaction. A series of carboxylate containing pyridinium-**TPHAP** derivatives was prepared and characterized by single crystal X-ray diffraction. The **Cu-pyridinium-TPHAP (Cu-NL 1)** network was successfully synthesized. The lowering of ICT transition energy in the pyridinium-**TPHAP** systems was beneficial for their ability to generate ROSs and enhanced the catalytic activity of heterogenous photooxidation of 1,5-DHN. Furthermore, after incorporation into the network structure, the photostability of the ligand was improved. At the same time, **Cu-NL 1** was shown to retain its structural integrity even after prolonged light irradiation.

In **Chapter 5**, the overall insights from the main **chapter 2 to 4** are summarized with outlook and future work that could help for further improvement of these research fields.

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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