



HOKKAIDO UNIVERSITY

Title	Study of Phenylazothiazoles as Visible-Light Photoswitches [an abstract of dissertation and a summary of dissertation review]
Author(s)	林, 潤澤
Degree Grantor	北海道大学
Degree Name	博士(生命科学)
Dissertation Number	甲第15776号
Issue Date	2024-03-25
Doc URL	https://hdl.handle.net/2115/91878
Rights(URL)	https://creativecommons.org/licenses/by/4.0/
Type	doctoral thesis
File Information	Runze_Lin_abstract.pdf, 論文内容の要旨



学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称 博士（生命科学） 氏 名 林 潤澤

学 位 論 文 題 名

Study of Phenylazothiazoles as Visible-Light Photoswitches
(可視光分子スイッチとしてのフェニルアゾチアゾール類の研究)

Photopharmacology achieving remote control of drug activity by light irradiation are under the spotlight as a new strategy to treat diseases with a high selectivity of drug. To contribute to the development of photopharmacology, there is a growing demand to develop new photoswitches with superior photoswitchability. Molecular photoswitches undergoing reversible conversion between *E* (*trans*) and *Z* (*cis*) states have attracted considerable attention and have been widely used in the fields of biology and chemistry. However, most reported photoswitches suffer from the drawback of a shortage in responsive wavelength of light. Here, we report a new collection of photoswitches, phenylazothiazoles (PATs), switching upon visible light irradiation for both directions with large conformational changes. The parent photoswitch, which comprises a five-membered thiazole heteroaryl segment directly connected to a phenyl azo chromophore, has very different spectral characteristics, such as a redshifted absorption maximum wavelength and well-separated absorption bands of the *trans* and *cis* isomers, than conventional azobenzene and other heteroaryl azo compounds. In total eleven molecules were designed and synthesized by introducing electron-donating or electron-withdrawing substituents to phenyl rings. Substituents at the *ortho* and *para* positions of the phenyl ring of the photoswitch resulted in a further shift to longer wavelengths up to 525 nm at the absorption maximum, which can be excited by red light irradiation. These photoswitches showed excellent photostationary distributions of the *trans* and *cis* isomers. Thermal half-lives of all molecules up to 7.2 h with electron-withdrawing substituent, while electron-donating substituent render a half-life time down to 2 s. Quantum yields of PATs were also studied, the results indicate high switching efficiency for all detectable molecules. For biology use, excellent reductant stability of *E* and *Z* isomers of most molecules was observed. The X-ray crystal structure analysis revealed that the *trans* isomers exhibited a planar geometry, and the *cis* isomers exhibited a T-shaped orthogonal geometry. Detailed *ab initio* calculations further demonstrated the plausible electronic transitions and isomerization energy barriers, which were consistent with the experimental observations. In conclusion, with the thiazole ring that endowing anticancer activity, PAT derivatives show favorable photophysical properties to be used as visible-light photoswitches in photopharmacology applications.