

# Enantiodifferentiating Photosensitization of Cycloalkenes using Nucleosides, Oligonucleotides, and Double Stranded DNA as Chiral Sensitizer/Environment

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ヌクレオシド・オリゴヌクレオチド・二重らせん DNA を

キラル増感剤／反応場とする

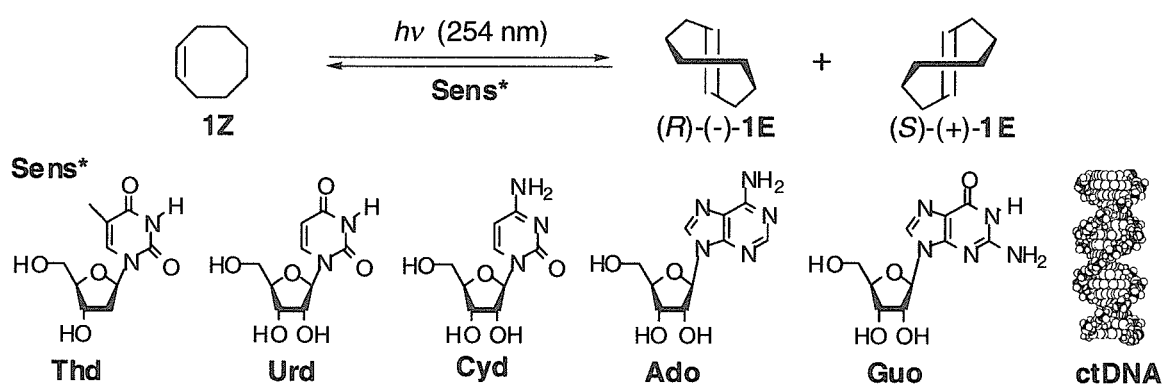
シクロオクテンの光増感不斉異性化反応

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Enantiodifferentiating photosensitization is an attractive chirogen-effective method for transferring molecular chirality in the electronically excited state.<sup>1</sup> Recently, we have demonstrated that moderate to good *ee*s are attained in the enantiodifferentiating photoisomerization of (*Z*)-cyclooctene (**1Z**) to the chiral (*E*)-isomer (**1E**) when sensitized by chiral (poly)alkyl benzene(poly)carboxylates.<sup>2</sup> In these studies, we have consistently employed arenecarboxylates as chiral sensitizers, in which the chirogenic center is separated by at least three C–C/C–O bonds from the aromatic chromophore. Nucleosides appear to be more promising as chiral sensitizers, since the optically active furanose moiety is directly connected to the chromophoric nucleobase in a more defined orientation. Furthermore, this approach may open a channel to the supramolecular asymmetric photosensitization with DNA used as a chiral sensitizing host in aqueous solution. Most of the investigations on the photochemistry of nucleic acids have been related to skin cancer research, while the photoinduced electron transfer through double stranded DNA (dsDNA) has attracted widespread interest in the last decade. Although photosensitized reactions and modifications of DNA/RNA have also been extensively investigated, nucleosides and DNA have rarely been employed as photosensitizers. Nevertheless, these biomolecules, possessing both chromophoric nucleobase and furanose units, should function as aqueous based chiral sensitizers, and more importantly the lipophilic helical grooves of dsDNA should provide the chiral environment for supramolecular asymmetric photosensitization.

In this first attempt to use nucleosides and dsDNA as chiral sensitizers/hosts, we employed the enantiodifferentiating photoisomerization of **1Z** as a bench-mark test system for examining their ability to transfer supramolecular chirality through the excited state interactions, since common nucleosides absorb around 260 nm UV light, emit weak fluorescence, and possess singlet energies around 410 kJ/mol, which are comparable to those of benzenecarboxylates and therefore expected to function as chiral photosensitizers. Thymidine and oligothymidylate, as well as calf thymus DNA, were shown for the first time to function as chiral photosensitizers in aqueous solution, to effect the enantiodifferentiating photoisomerization of **1Z**, giving the chiral **1E** in ee s of up to 21, 29, and 15%, respectively.



**Scheme 1.** Photoisomerization of (*Z*)-cyclooctene sensitized by nucleosides and ctDNA

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