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Title of Doctoral Dissertation

Dynamic Induction of Enantiomeric Excess from a Prochiral Azobenzene Dimer
under Circularly Polarized Light
(円偏光によるプロキラルアゾベンゼン二量体からの鏡像異性体過剰の動的誘起)

Homochirality in Nature is one of the great unsolved and intriguing topic that has attracted the scientists for a long time, for which many experiments and theories have been reported. Among the several physical sources that have been proposed to achieve enantiomeric imbalance in molecular systems, circularly polarized light (CPL) is the most studied chiral physical field, considering the role of interstellar CPL in initial enantiomeric bias, and seems to be the strongest candidate for explaining the biomolecular homochirality that exists in Nature. Thus, enantiomeric enrichment of organic compounds through the action of CPL continues to be an area of high research interest.

There are three CPL-induced reactions according to the manner of enantioselective conversion occurs: photodestruction, photoresolution and absolute asymmetric synthesis, however, an unequivocal classification is sometime not possible. The main difference between the photoresolution and absolute asymmetric synthesis is whether the chirality itself is generated during the photoreaction or not. In photoresolution, the starting compound is usually racemic mixture of a chiral molecule, which can be converted reversibly to its antipode through a photochemical path. Such reversible enatio-differentiating photoisomerization of chiral molecules using CPL based on the preferential interaction of *r*- or *l*-CPL with one of the enantiomers is known for some compounds. In contrast, only one example of asymmetric synthesis with CPL has been reported: photochemical conversion of diarylolefins to chiral helicene derivatives with an enantio-imbalance under CPL.

The dynamic generation of point and planar chirality in compounds **1** and **2**, respectively, upon conformational changes caused by *E*-*Z* photoisomerization of one of their azobenzene units have been reported recently. To apply this novel concept in an axially chiral system, in this dissertation, I present a novel design **3**, which features two phenylazo groups at the ortho positions of phenyl ring substituted by a naphthyl moiety and then investigated the possibility of photoinducing enantiomeric excess using **1**, **2** and **3** under CPL. Irradiation of **1-3** with light induced *E*↔*Z* photoisomerizations of their azobenzene moieties, giving mixtures of their *EE*, *EZ*, and *ZZ* isomers in the photostationary state (PSS). Among these regioisomers, the *EZ* forms are chiral and existed as racemic mixtures of *R* and *S* stereoisomers. Upon CPL irradiation of **3**, circular dichorism (CD) revealed enantiomeric enrichment of one of the *EZ* stereoisomers; furthermore, irradiation with *r*- or *l*-CPL gave CD signals opposite in sign, but with equal intensity, in the PSS. In contrast, **1** and **2** did not give any detectable induced CD upon CPL irradiation. These experimental results can be explained by considering the different Kuhn anisotropy factors (*g*) of the (*R*)-*EZ* and (*S*)-*EZ* stereoisomers of **1-3**, assuming that the origin of the enantiomeric excess is the enantio-differentiating photoisomerization from *EZ* stereoisomers to nonchiral *EE* or *ZZ* regioisomers by *r*- or *l*-CPL.

In this study, I introduce a new concept, in which enantiomeric induction occurs from a prochiral azobenzene dimer through *in situ* formation of a chiral structure upon CPL irradiation at a suitable single wavelength. I propose a new absolute asymmetric synthesis, where enantiomeric imbalance is obtained as a result of an enatio-differentiating photoisomerization path from the photochemically formed enantiomers for one chiral regioisomer (*EZ*) to a common ground state of its other non-chiral regioisomers (*EE* or *ZZ*).

If absolute asymmetric synthesis is defined as the reaction of an achiral compound to give a chiral product without any sources of chemical chirality, our present CPL-induced reaction for **3** to form a chiral product with enantio-imbalance is seemingly a new asymmetric photosynthesis using CPL. Actually it is a simultaneous photoresolution process of a photochemically formed racemic mixture.

This is the first demonstration of simultaneous generation of asymmetry and photoresolution in a single molecule under CPL irradiation. I believe that such a chiral-to-nonchiral enantio-differentiating photoisomerization pathway upon irradiation with *r*- or *l*-CPL constitutes a molecular model, involving a partial photoresolution mechanism, that might explain the chiral imbalance found in Nature. I also anticipate that *in situ* generation of chirality from prochirality through the action of light, without any complex chemical reactions; will be a promising method for operating optical memory devices.