

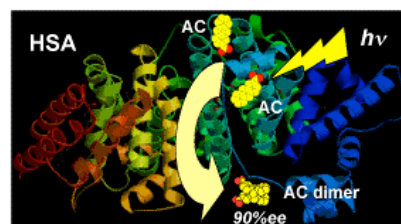
Novel Strategy of Supramolecular Asymmetric Photochirogenesis with Tailor-made Biopolymers as Chiral Reaction Media and Development of High Sensitive and High Time-Resolve Circular Dichroism (CD) Detection Method for Analysis of Supramolecular Dynamics



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Increasing attention has recently been directed toward the new methodology of asymmetric photochemistry using various supramolecules as chiral reaction medias. In this paper, we will present the novel strategy and recent results of supramolecular asymmetric photochirogenesis (SMAP) with tailor-made biomolecules, such as polymer modified proteins polymer-protein hybrids), synthetic antibody, and DNA/RNA aptamers as chiral reaction medias.



The biopolymers, especially proteins, possessing chiral binding pockets for guest, are of particular interest as potential chiral reaction cavities and/or fields for SMAP, although such an approach has not extensively been investigated. Serum albumins are the most abundant and well-characterized water-soluble plasma proteins, which transport hydrophobic compounds. We have employed Bovine, Human, Porcine, Canine Serum Albumin (BSA, HAS, PSA, CSA) as a chiral supramolecular photoreaction media and 2-anthracenecarboxylate (AC) as a substrate. The photocyclodimerization of AC was performed in aqueous buffer solutions in the presence of CSA to give the [4+4] cyclodimers with high enantioselectivities of up to 96% ee and PSA to give the antipodal AC dimer with up to 90% ee. However, little is reported about the positive design and active control of supramolecular photochirogenesis with biomolecules used as chiral environment for reaction.

Recently synthetic (catalytic) antibody is one of the most powerful and vital tools for thermal reactions. In this strategy, variety of reaction intermediates are used as antigens, which called as hapten, and then antibodies produced can be used as effective catalysts. Therefore, synthetic antibody possessing chiral binding pockets for AC cyclodimers, are of particular interest as potential chiral hosts for SMAP, although such an approach has not extensively been investigated. In this paper, we will present first supramolecular photochirogenesis using synthetic antibody as tailor-made chiral reaction fields. Additionally, we will present possibility of polyethylene oxide modified serum albumins also as tailor-made chiral reaction medias of SMAP.

Chirality on supramolecular systems is quite informative for us to know their structures because it is sensitive to the local arrangements of the host and guest molecules in supramolecular systems.

In the supramolecular systems, a chiral molecule as a host and achiral molecule as a guest and vice versa, may give a chiral supramolecule. It is considered that the dynamics of chirality in chiral supramolecular systems directly indicate the formation of the supramolecules and the structural fluctuation of them; therefore, we expect that the detection of the chiral dynamics in the supramolecular system will open a new door to the supramolecular chemistry based on its structure.

It is well-known that circular dichroism (CD) is the major tool for investigating the chirality, however, the dynamic information of chiral systems from CD measurements are poor because of the limitation of time-resolution based on the instrumentation. In other words, the improvement of the time-resolution of CD measurements may be quite fruitful for us to understand the dynamics in supramolecule's formation and fluctuation. Moreover, Improvement of the time-resolution of CD will help us to measure the excited state chiral dynamics in chiral supramolecular systems for understanding the photophysical and photochemical events appearing in them. Based on a pioneering work shown in a literature [1], we have been continuing to develop time-resolved CD spectroscopy. Firstly, to check our experimental setup (validity of the CD spectrum and time-resolution of our setup), we detected the laser-induced CD change in the supramolecular system as Zn-porphyrin dimer (host) recognizing the chiral small molecule as a guest [2]. In this system, we observed a decrease of the ground state CD signal without any CD spectra change just after ns-laser irradiation. In decaying the T-T absorption of porphyrin chromophore, the ground state CD signal was recovering to the initial intensity. This phenomenon may be explained by the following; the decrease of ground state CD was attributed to the lack of ground state due to the excited triplet state generation and no CD spectra change meant any significant structural change of the supramolecules in the observed timescale. Furthermore, we may conclude that our setup potentially has a several μs or more less time resolution in this experiment.

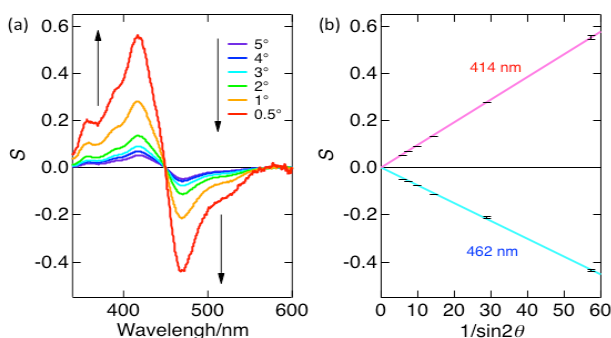


Figure 1 The S spectra of $\Delta\text{-Ru}(\text{bpy})_3\text{Cl}_2$ with various azimuth of retardar (a) and plots of S values against the inverse of $\sin^2\theta$ at 414 and 462 nm (b).

- 1) Nishijima, M.; Goto, M.; Yang, C.; Mori, T.; Wada, T.; Inoue, Y. Chem. Commun. 2014, 50, 14082.
- 2) Murakami, M.; Araki, Y.; Sakamoto, S.; Hamada, Y.; Wada, T., Chem. Lett. 2013, 42(3), 261-262 (Editor's Choice).