Dynamic redox systems with a function of chiral memory:
Electrochemical control of racemization barrier of dibenz[c,e]oxepine skeleton

Takanori Suzuki,1 Kazuhisa Wada,1 Yusuke Ishigaki,1 Yasuyo Yoshimoto,1 Hidetoshi Kawai,1,2 and Kenshu Fujiwara1

1Department of Chemistry, Faculty of Science, Hokkaido University
2PRESTO, Japan Science and Technology Agency, Japan

Chiral amplification is an interesting event of supramolecular chirality transfer. One of the representative modifications is shown in Scheme 1, where the easily interconvertible enantiomers [(±)-A, racemic mixture] is transformed into another chiral molecule B in favor of one handedness by the aid of a small amount of chiral catalyst (cat*). The success of this process relies on the diastereomeric preference in forming the complexes of (+)-A•cat*/(-)-A•cat*, as well as the drastic increase of racemization barrier upon transformation of A to B.

As shown in Scheme 2, when the chiral product B with stable configuration can be reconverted into the starting material A through another reaction, the chiral information of compound B induced by cat* would be disappeared. Thus, the molecular system of (±)-A and (+)-B/(-)-B can store and erase the chiral information induced by cat*, which can be considered as “chiral memory”. By adopting our own concept of “dynamic redox systems”, we have succeeded in constructing the novel redox pair (P)/(M)-1 and (P)/(M)-22+, which act as the chiral memory shown in Scheme 2.

We have designed here dication 22+ with the 5, 7-dihydrodibenz[c,e]oxepine skeleton, that would not undergo ring flip due to the steric bulkiness of the two diarylmethylum units at 1,11-positions. We also assume that the C-C bond formation between the two carbenium centers upon reduction of 22+ drastically reduces the racemization barrier in 1 (Scheme 3). Due to the electrochemical bistability for the “dynamic redox systems”, the electron exchange between 1 and 22+ must be suppressed, thus the optically pure 22+ would be available just by increasing the racemization barrier in 22+. 
4-Methoxyphenyl group (An) was selected as aryl groups to stabilize the dicationic state, and \(2a^{2+}\) was prepared over two steps from 1,11-dibromo-5,7-dihydrodibenz[c,e]oxepine via diol 3a and isolated as stable BF\(_4^-\) salt (Scheme 4). Reduction with Zn powder gave the hexaphenylethane-type compound 1a as a stable colorless solid, which adopts the helical geometry as determined by X-ray analysis (Fig. 1). The VT-NMR analysis showed that the \(\pi\)-framework in 1a undergoes rapid ring flip (\(\Delta G^\ddagger = 16 \text{ kcal mol}^{-1}, k = 22.5 \text{ s}^{-1}\) at 298 K). In contrast, no racemization occurs in the dicationic state (\(\Delta G^\ddagger > 25 \text{ kcal mol}^{-1}\)) since the circular dichroism spectrum of optically pure \(2a^{2+}\) obtained from the resolved diol 3a remained unchanged even after 48 hours (Fig. 2), thus confirming the successful construction of chiral memory system shown in Scheme 2. Further studies are now in progress to realize the chiral amplification process by using the present molecules.

Scheme 4

![Fig. 1 X-ray Structure of 1a](image1)

![Fig. 2 CD spectrum of resolved 2a^{2+} (BF\(_4^-\))\(_2\) in CH\(_2\)Cl\(_2\)](image2)

**Name**: Kazuhisa Wada

**Position and Affiliation**: Bachelor of Science, Hokkaido University

**Postal Address**: North 10, West 8, Kita-ku, Sapporo 060-0810, Japan

**Phone/Facsimile**: +81-11-706-2713/+81-11-706-2714

**Email**: k-wada@mail.sci.hokudai.ac.jp

**Academic Background**:

2009.3 B.S., Hokkaido University, Hokkaido, Japan

2009.4- M.S., Hokkaido University, Hokkaido, Japan