

# Molecular Switches of a Self-Assembling Helical Biladienone

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## ABSTRACT

A molecular switch prepared from zinc biladienone with long alkyl chains dissolved in 5CB showed multi-negative differential resistance (NDR) when gate voltage was applied, while a molecular switch prepared from zinc biladienone in THF showed no NDR, although the conductance was six orders of magnitude higher in the latter molecular switch.

**Keywords:** conformational change, reversal of polarization, multi-negative differential resistance

## 1. INTRODUCTION

Since there are many problems in manufacturing nano-scale devices for a molecular switch, many electrodes must be produced before there is a sufficient yield to allow molecular switches to be judged to meet production standards. Using e-beam lithography, it is currently possible to produce a substantial supply of electrodes with a 10 to 20 nm gap for molecular switches. Thanks to these highly reliable electrodes, we report here new molecular field-effect switches employing zinc biladienone (C12\_Zn) as an active element.

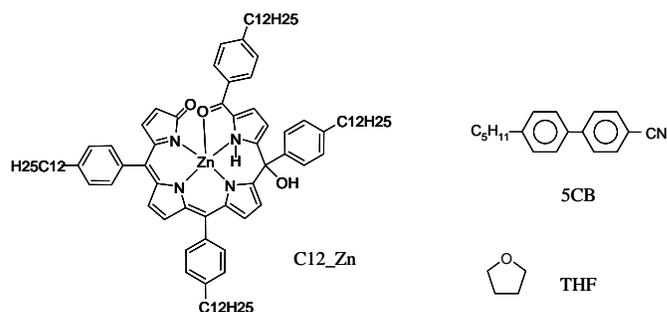


Fig. 1 Structures of zinc biladienone, 5CB and THF. The dipole moments of 5CB and THF are 4.05D [1] and 0.7D, respectively.

Many attempts have been made to develop a molecular switch using disk-shaped molecules bearing long alkyl chains such as porphyrins, phthalocyanines [2], and hexabenzocoronenes [3], with particular attention being paid to the self-assembling property of these compounds. While these compounds have a rigid core structure, C12\_Zn has a non-symmetric flexible structure. Figure 1 shows the structure of C12\_Zn, bearing a dodecyl group on the peripheral phenyl groups. The core structure of C12\_Zn is discotic, similar to that of porphyrins. In contrast to porphyrins, C12\_Zn has a discontinuous structure in its  $\pi$ -electron system with an sp<sup>3</sup> carbon at the meso position, and adopts a flexible helicoidal conformation [4]. Because linear tetrapyrroles with a similar structure are found in photoreceptor proteins, we expect that biladienones are applicable to a switching device by utilizing their flexible conformation [4].

## 2. EXPERIMENTAL

C12\_Zn was prepared from the corresponding free base biladienone by a reaction with zinc acetate. For the preparation of the free base, see Yamauchi et al. [5]. Measurements were made using a semiconductor parameter analyzer (Agilent 4156B) with a nanoprobe system (Nagase Electronic Equipments Service Co., Ltd. BCT-11MDC-4K). The samples were subjected to a programmable bias voltage. The nanoprobe system is equipped with a hermetically sealed sample chamber which is flushed with nitrogen to minimize oxygen and water-vapor contamination. Two kinds of molecular switches of C12\_Zn were prepared from 2-mM solutions of either 4-pentyl-4'-cyanobiphenyl (5CB) or tetrahydrofuran (THF). The 1-microL solutions were deposited between 16-nm-gap gold electrodes, with 5-nm-thick Cr and 20-nm-thick Au layers made using e-beam lithography, onto a doped Si substrate with a 70-nm-thick SiO<sub>2</sub> insulator, as shown in Fig. 2. The molecular switch from the 5CB solution was stored for seven days, then the 5CB solvent was distilled under vacuum at room temperature. The molecular switch from the THF solution was stored under saturated THF vapor pressure for seven days, then the THF solvent was evaporated over 24 hours. Before electrical measurements, both samples had bias voltage from -2V to +2V applied in 40 steps with an increment of 50mV over two hours in order to orient the molecules.

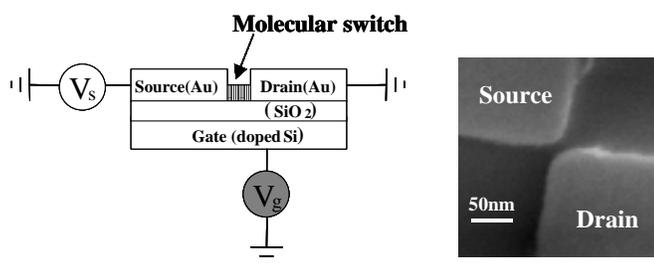


Fig. 2 A schematic diagram of the molecular switch device with an inset showing an SEM image of the electrode with a 16 nm gap

## 3. RESULTS AND DISCUSSION

The current-voltage curve of the molecular switch from the 5CB solution is shown in Fig. 3 (a). Without gate voltage applied, two negative differential resistance (NDR) curves showed the symmetry of positive- and negative-bias voltage. When negative gate voltage is applied, two additional NDR peaks appeared in the lower bias-voltage region. When positive gate voltage is applied, no NDR peaks were observed (data not shown).

The I-V curves of the sample from the THF solution before gate voltage was applied are shown in Fig. 3 (b). These curves are clearly nonlinear and asymmetrical. Beyond bias voltage of 3 V, the current rises sharply and if higher voltages are applied, the I-V curves do not show reproducibility. The current of this sample from the THF solution is of a microampere-order, that is, six orders higher than that of the sample from the 5CB solution. In addition, there was hysteresis in the rising and falling I-V curves of bias voltage. When gate voltage was applied, these profiles did not show a significant change, although there were slight changes in their gradients. When +2 V gate voltage was applied, the ratio of on to off is only 1.2. (The bias voltage was +2.5 V.)

The difference between the I-V curves in Fig. 3 (a) and (b) shows that using the solvent in the sample-making process affects the molecular orientation. In order to elucidate the difference in the molecular orientation of the 5CB and THF solutions, we focused on the molecule association of solvent to the C12\_Zn. In the previous paper, Kita et al. reported that the molecule association of the solvent to zinc biladienone regulates its aggregation. The dehydration reaction of C12\_Zn followed the first order kinetics in the C12\_Zn concentration both in the 5CB and THF, suggesting that the 5CB and the THF associate to the C12\_Zn to eliminate aggregation of C12\_Zn. This result means that molecular orientation in a molecular switch is decided by C12\_Zn associated with 5CB or THF molecules [6]. As shown in Fig. 1, the volume of 5CB molecules is different from that of THF molecules. Because a

bulky 5CB molecule is associated with the C12\_Zn molecule, there is a long distance between adjacent C12\_Zn molecules, so C12\_Zn molecules cannot form  $\pi$ - $\pi$  stacks. Although we have devised a process to remove solvent molecules from the solution, complete removal is very difficult at the molecular level. Because the intermolecular interaction of C12\_Zn molecules with 5CB molecules is different from that with THF molecules, the molecular orientation of C12\_Zn molecules must also be different. A difference in orientation means that the conductance of the molecular switch and the degree of change in the conformation and/or the molecular orientation caused by the application of a gate voltage must be remarkably different. Because C12\_Zn has some groups having dipole moments and 5CB molecules have a high dipole moment [1], if 5CB molecules remain, the 5CB associated with C12\_Zn must have a high dipole moment [7]. An NDR pair without gate voltage in the I-V curve of a C12\_Zn element from a 5CB solution, as shown in Fig. 3 (a), is caused by a reversal of polarization similar to that in ferroelectric liquid crystals. With gate voltage applied, the molecular structure and/or orientation changes, and this change produces the multi-NDR.

The conductance of the molecular switch from the THF solution was higher than that from the 5CB solution, as is shown in Fig. 3 (b). This conductance is equivalent to that of a 2nm-long conjugate molecular system with double thiol groups connected to gold electrodes [8]. Using infrared-reflectance-absorption spectroscopy of C12\_Zn on a gold film on glass we found, contrary to our expectations, that C12\_Zn lies on the surface of the gold electrode due to adhesion between the alkyl chains and the surface [9]. If the contact resistance between the C12\_Zn molecules and the surface of the electrode is equivalent to that between S in thiol and Au in the electrode in the conjugate molecular system of Reichert et al. [8], the conductance through multiple C12\_Zn molecules (not through a single molecule as in our case is with a 16nm-long gap) is too high. The foregoing is evidence

that there are multiple conductive pathways for electron transport in C12\_Zn and that the electrical properties in these pathways are similar each other and show good reproducibility.

Nevertheless no NDR was seen in the I-V curve of C12\_Zn from the THF solution, as is shown in Fig. 3 (b). The existence of polarization is suggested, because there is hysteresis between the rise and fall bias voltages. However, considering that there is no polarization reversal and no change in the I-V profile with gate voltage applied, we think that the molecular structure and/or orientation is difficult to change by applying bias and gate voltages.

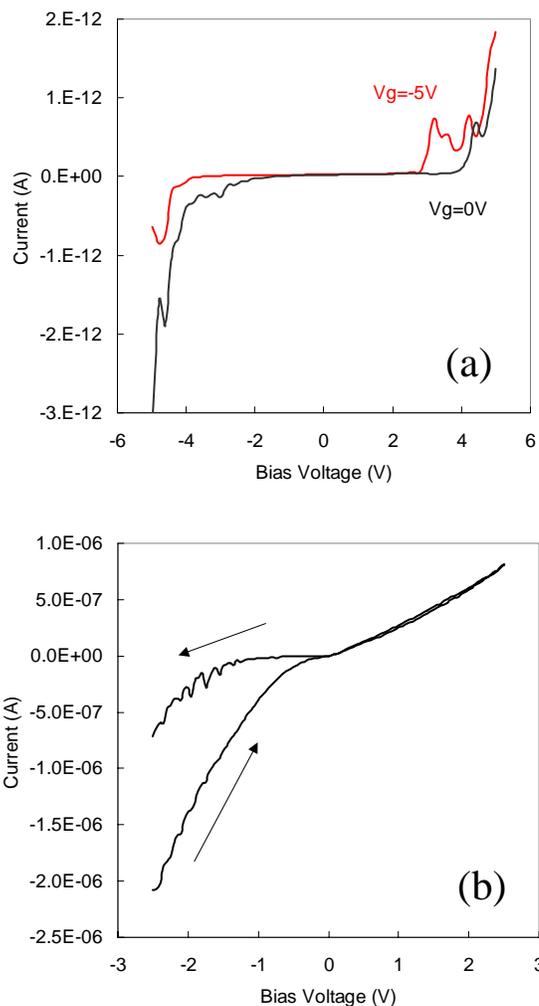


Fig. 3 (a) I-V curve of C12\_Zn from the 5CB solution (b) I-V curve of C12\_Zn from the THF solution

## 4. CONCLUSION

Two different I-V characteristics of C12\_Zn switching elements prepared from two kinds of solvent were found. The I-V curve of the C12\_Zn molecular switch prepared from the 5CB solution showed NDR caused by a reversal of polarization. With gate voltage applied, the molecular structure and/or orientation changes, and this change produces the multi-NDR. The C12\_Zn molecular switch prepared from the THF solution, however, has multiple conductive pathways for electron transport and showed high conductivity. We consider this difference comes from the difference in molecular orientation.

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[6] K. Kita, T. Tokuoka, E. Monno, S. Yagi, H. Nakazumi and T. Mizutani, *Tetrahedron Lett.* 47, 1533, 2006. Kita et al. reported that it depends on the solvent whether C12\_Zn forms a monomer or a dimer in solution. Because the difference does not depend on whether the solvent is polar or nonpolar. Either the monomer conformation or dimer explains whether the solvent molecules are associated or not with the C12\_Zn.

[7] Based on ab initio molecular orbital simulations (B3LYP/6-31G(d)), the angle between the permanent dipole moment of C12\_Zn and the plane defined by three nitrogen atoms in conjugated pyrrole units was calculated to be 12.1°.

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