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NLO分子スイッチの超分極率増大に関するThrough-Space/Bond 軌道間相互作用解析

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Through-space/bond interaction analysis on NLO properties enhancement of molecular switches

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Recently, the nonlinear optical materials with controlled switching properties draw a lot of interests, because such kinds of materials are good candidates for optical information storage devices, and photoresponsive materials, as well as biosensors. A good NLO switch should exhibit an enough large difference of the response between the two states. To date, a variety of the NLO switches have been designed and investigated experimentally and theoretically [1-2]. There are several kinds of the molecular switches, of which, the transformation can be caused by the acidochromes or photochromes, and so on. In this work, we focus on the acidochromic induced tunable NLO switches, closed form (CF) and open form (OF) of (10-ethenyl-indolino[2,1-b]oxazolidines), as shown in Fig. 1. When the pHs of the environments change, the structures of the acidochromic compounds are tuned. The transformation of the structures can be detected by comparing the absorption spectra. Although the designs and investigations of the mechanisms are increasing, the further deep investigations of the mechanism are still on the way.

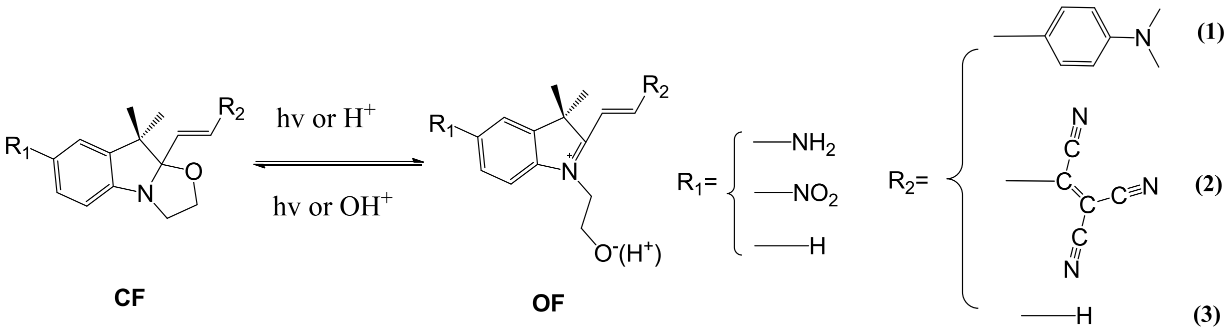

Fig. 1 The switching procedures of target molecules (10-ethenyl-indolino[2,1-b]oxazolidines).

This mechanism of the switchable properties can be examined through orbital interaction perspective. The concept of through space/bond (TS/TB) orbital interaction which was originally proposed by R. Hoffmann, et al.[3], is very useful in demonstrating the mechanism of the stereoelectronic effects and charge transfer. Our group developed the TS/TB orbital interaction analysis in ab initio level[4], in this analysis, the interactions between orbitals are estimated quantitatively. The procedure of the TS/TB orbital interaction analysis in *ab initio* level is by modifying the exponent α of the Gaussian-type orbitals ($\exp(-\alpha r^2)$) in the basis-sets. In the procedure, the estimation of the interaction between hydrogen-like atoms A and B was considered as an example (Fig. 2(a)). AOs r and s belong to atoms A and B, respectively. The absolute magnitude of the exponents in the Gaussian-type functions related to the interaction between r and s should be increased gradually until orbital overlap is completely eliminated. And the π-π interaction is deleted as shown in Fig. 2(b). The finite-field(FF) method has been applied for the (hyper)polarizabilities calculations. All the molecules are optimized at HF/6-31G(d), and the polarizability and first hyperpolarizabilities are also calculated at HF/6-31G(d) in GAUSSIAN 09.

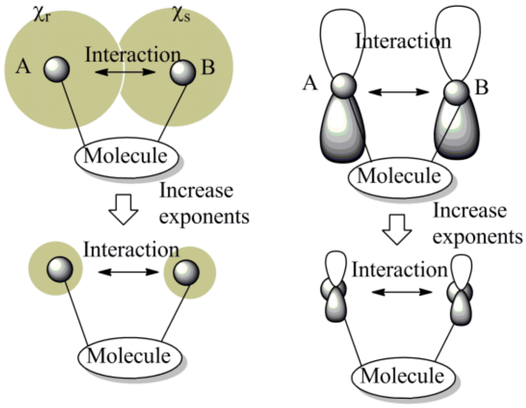

Fig. 2 The procedure of TS/TB orbital deletion.

For the OF system as shown in Fig. 3, the first hyperpolarizability β is 6300.49 au. The β of the CF is 712.99 au. The ratio of the β between OF and CF is 8.84 (OF/CF). The big ratios of the hyperpolarizabilities between CF and OF suggest that these kinds of molecules will be a good candidate for the molecular switches.

There are two assumptions of the effects that cause the big difference of the hyperpolarizabilities between CF and OF. One of the factors causing the large hyperpolarizability of OF may be from the electron transfer (see Fig.3(a)) , another one may be come from the interaction between the cation and anion formed after the ring is open (see Fig.3(b)).

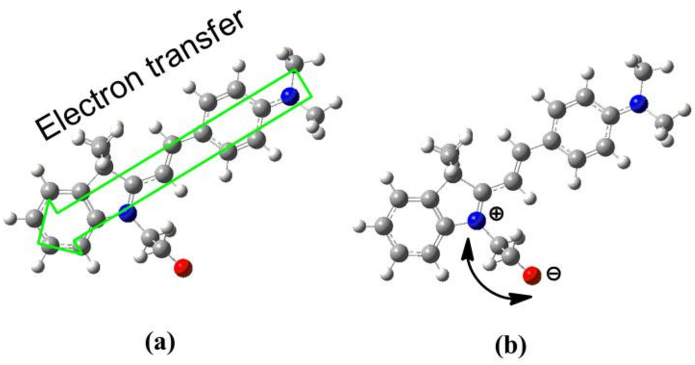

Fig. 3 (a) The electron transfer along the backbone of OF, (b) electron interaction between the anion and cation in the OF.

The mechanism of the enhancement of the hyperpolarizabilities of OF molecules is analyzed by evaluating the TS/TB orbital interactions. The investigations are still on the way.

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