Linear and Cyclic vinylogous TTF: Molecular movement induced by Electron Transfer

M. Guerro, R. Carlier, D. Lorcy and P. Hapiot
Synthèse et Electrolyse Organiques, Institut de Chimie de Rennes. Campus de Beaulieu, Bât. 10 C; F-35042 Rennes, France, e-mail: philippe.hapiot@univ-rennes1.fr

Molecules where molecular movements can be triggered by simple electron transfer are the focus of much attention for the design of molecular devices (switches, motors, sensors,...). The control of the extend and nature of the conformational changes are one of the principal challenges to achieve this goal. Within this frame, we have prepared a series of vinylogous tetrathiafulvalenes (TTF) by oxidative coupling of 1,4-dithiafulvenes. This interest in these molecules is related to the ability of this method for introducing various substituents (R) on the central conjugation. The presence of the bulky substituents R does not modify the donor ability of the molecules but the donor cannot be planar due to the steric interactions, inducing large molecular movements associated with the electron transfers. Depending on the steric hindrance and the donating (or withdrawing) character of R, the oxidation of the TTF occurs either through a reversible bielectronic transfer leading directly to the dicationic state or through two reversible monoelectronic transfers corresponding to the consecutive formations of the cation radical and of the dication. These different electronic behaviors were investigated by cyclic voltammetry in acetonitrile and dichloromethane and interpreted with the help of density functional theory calculations (B3LYP).

The use of a link connecting the dithiole rings through the outer sulfur atoms of the vinylogous TTF (molecule 2) core modifies marginally the donor ability. This additional steric strain induces different conformational changes upon oxidation than the stretch one observed for the unlinked vinylogous TTF 1. The cyclic vinylogous TTF 2, with a short bisthioalkyl link, act as a fast and reversible molecular clip that can be closed by electron transfer. The movement appears to be almost insensitive to the nature of the substituents or its steric hindrance on the central conjugated spacer between the two dithiole rings. For instance, the phenyl rings remains in a twisted position in all the redox states and therefore do not interfere in the closing of the molecular clamp. The introduction of various substituents, other than phenyl groups is possible on the central conjugation according to the chemical pathway used to reach these cyclic vinylogous TTF. For future uses of these systems in molecular engineering, this can be an advantage, as the presence of functional substituents, in order to prepare a trap or a sensor, should not change the nature of the molecular movement. Moreover, this procedure appears as an easy way, with regard of the quantity (gram scale) and the simplicity of the synthesis, to novel molecular clips triggered by electron transfer.

References