

Highly efficient photoswitch in diarylethene-based single- and bilayer molecular junctions

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<u>Abstract:</u> Photochromic molecules, that is, molecules with two different forms (open/non conjugated and closed/conjugated) which can be interconverted by light irradiation, have been proposed as building blocks for photoresistive switches in molecular electronics¹. Diarylethenes (DAE) are among the molecules that have been extensively investigated due to their excellent properties such as the high reversibility, thermal stability and fatigue resistance of both forms. Most studies, investigating the transport characteristics of photochromic molecules, are devoted to monolayers or single-molecule-based Molecular Junctions (SMJs) where the dominant transport mechanism is direct tunneling. Hopping transport, whichhas a stronger molecular signature, has remained almost unexplored. Herein we present the electrical characterization of photoswitchable MJs using molecular layers of diarylethene oligomers (oligo(DAE)) for tunneling and hopping transport regimes.

First, we prepared single-layers of the oligo(DAE) deposited by electrochemical reduction on gold electrodes with several thicknesses. The layers were fully characterized using electrochemistry, XPS, and AFM. The electrical characterization of closed and open forms of oligo(DAE) were investigated by C-AFM and will be presented for two different layer thicknesses fixed at 2-3 nm and 8-9 nm, i.e. below and above the direct tunneling limit. It was observed that both layers switch between high and low conductance modes ("ON" and "OFF" states corresponding to "closed" and "open" forms of the oligo(DAE), respectively) when irradiated by UV and visible light, respectively. ON/OFF ratios of 2-3 (Fig.1.A) and 200-400 (Fig.1B) were obtained for 3 nm- and 9 nm-thick DAE MJs, respectively².

Next, we prepared, using a bi-layer system, 9 nm-thick MJs, i.e. in the hopping transport regime. The first layer (5 nm) is based on bisthienylbenzene oligomers, (BTB). The second layer (4 nm) is based on the oligo(DAE). The impact of this first layer on the switchable properties of the system and on the electronic behavior and on the photoresponse of the 9 nm-thick DAE-based MJs will be presented, with focus on its influence on the ON / OFF ratios (Fig.1C). Unprecedented ON/OFF ratio of 10000 at 1V were observed.³



Fig.1. Log(I) versus V characteristics before (green) and after (red) UV irradiation of (A) DAE_{3nm}, (B) DAE_{9nm}, and (C) DAE_{4nm}/BTB_{5nm} junctions measured by C-AFM.

References:

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