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Electronic memory devices based on the chalcone with negative electrostatic potential regions

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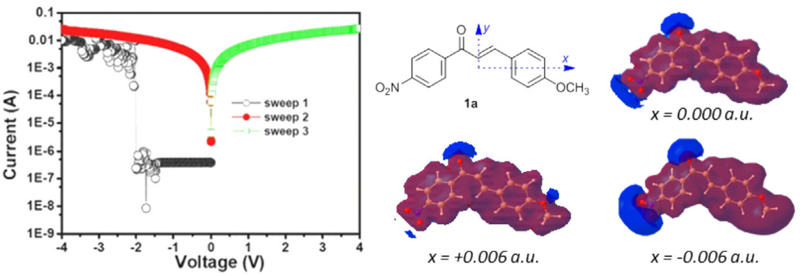
HIGHLIGHTS

- The molecular electrostatic potential (ESP) properties were used.
- The chalcone compounds were used for the WORM type device.
- The molecular geometries were optimized by the addition of a changeable electric field in the *x* direction.
- The structure–property relationship was discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

The molecular electrostatic potential (ESP) properties were used for the explanation of organic electric memory ability. Several chalcone compounds, owning a negative ESP region locates at the oxygen atom, were selected in this paper to validate the selection of compounds for organic memory materials. The synthesis, characterization, fabrication of the organic memory devices and the electrical properties for them were reported, and they were shown as WORM (write once read many times) type memory devices. The molecular geometries were optimized by the addition of a changeable electric field in the *x* direction inside the molecules using FF-DFT (Finite Field-Density Functionary Theory) method. The relationship between ESP of the molecules under different electric field and the property was discussed, and the mechanisms associated with the memory effect were also elucidated from DFT calculation results.

1. Introduction

The memory devices based on organic materials were well developed in the last decade. The researches in this field were mainly focused on the polymers with electron-withdrawing (acceptor, A) and electron-donating (donor, D) groups in the main or branching chains [1–9]. It was believed that the electron or hole injection would be more favorable in the D–A type polymers, in which the hybridization of the energy levels of the donor and acceptor moieties results in D–A systems with unusually low highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) separation [9]. Ree [10] and Lu [11] reported the electric properties of the polymer based on the unique monomer. The results indicate the other selection for organic materials served as the electric memory devices from the polymers which were prepared by the monomer with donor and acceptor parts.

The first report of the small organic molecule for electrical bistable devices was reported by Yang [12]. But it was not given enough attention until the recent discovery of the small organic molecule for the electric memory materials. Song reported the electric storage properties of triphenylamine type compounds by the scanning probe microscopy technology [13,14]. A ternary data-

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storage device based on the azo compounds was reported by Lu [15]. These results indicate the organic compounds with small molecular weight would be potential candidates for the electrical memory devices.

The above mentioned and related [16–21] researches were displayed the remarkable properties of their memory devices. However, the structural characteristic of the potential structures for device is still undiscovered. The molecular electrostatic potential (ESP) properties were used by several research groups for the explanation of electric abilities in the organic materials [15,22,23], the negative parts of the ESP, which were looked as the traps, would prohibit the transfer of the electrons. To validate the selection of compounds for organic electrical memory materials, the simple structures of chalcone with negative ESP regions are selected in this paper, and the synthesis and electrical properties are discussed in following with details.

2. Experimental

2.1. Synthesis

2.1.1. Materials and general methods

Starting materials were purchased from TCI (Shanghai) Development Co., Ltd. All analytic grade solvents (A.R.) were obtained from commercial suppliers and used directly. Nuclear magnetic resonance spectra were recorded on Varian Inova NMR spectrometers (400 MHz). TMS was used as an internal standard for ^{1}H NMR. High resolution mass spectra were obtained on a GC-TOF Mass instrument. Metaling points were determined on an X-4 microscope electron thermal apparatus (Taike, China).

2.1.2. General procedure for the synthesis of chalcone

To a stirred solution of the substituted aromatic aldehyde (10.0 mmol) and ketones (10.0 mmol) in approximately 20 ml of ethanol with an ice-water bath, a solution of 10% aqueous sodium hydroxide (10.0 mL) was slowly added drop wise via a self-equalizing addition funnel. The reaction solution was allowed to stir at room temperature for approximately 8 h. A precipitate formed was collected by suction filtration. Recrystallization from the appropriate solvent afforded the pure product.

*2.1.2.1. 3-(4-Methoxyphenyl)-1-(4-nitrophenyl)prop-2-en-1-one (**1a**).* Recrystallized from acetic anhydride to afford pale yellow crystals. Yield: 45%, m.p.: 175.6–176.6 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ(ppm): 8.34 (d, $J = 8.5$ Hz, 2H), 8.13 (d, $J = 8.5$ Hz, 2H), 7.82 (d, $J = 15.6$ Hz, 1H), 7.62 (d, $J = 8.5$ Hz, 2H), 7.36 (d, $J = 15.6$ Hz, 1H), 6.96 (d, $J = 8.5$ Hz, 2H), 3.87 (s, 3H). ESI$^+$ m/z: calcd for $C_{16}H_{14}NO_4^+$[**1a** + H]$^+$: 284.0917, found: 284.0927.

*2.1.2.2. 3-(4-Methoxyphenyl)-1-(3-nitrophenyl)prop-2-en-1-one (**1b**).* Recrystallized from ethanol to afford pale yellow crystals. Yield: 50%, m.p.: 173.4–175.1 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ(ppm): 7.88 (d, $J = 8.4$ Hz, 2H), 7.79 (d, $J = 15.6$ Hz, 1H), 7.62 (dd, $J = 12.7, 8.6$ Hz, 4H), 7.36 (d, $J = 15.6$ Hz, 1H), 6.94 (d, $J = 8.7$ Hz, 2H), 3.86 (s, 3H). ESI$^+$ m/z: calcd for $C_{16}H_{14}NO_4^+$[**1b** + H]$^+$: 284.0917, found: 284.0927.

*2.1.2.3. 1-(4-(Dimethylamino)phenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (**1c**).* Recrystallized from ethanol to afford pale yellow crystals. Yield: 51%, m.p.: 127.1–128.2 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ(ppm): 8.01 (d, $J = 9.0$ Hz, 2H), 7.76 (d, $J = 15.5$ Hz, 1H), 7.60 (d, $J = 8.7$ Hz, 2H), 7.47 (d, $J = 15.6$ Hz, 1H), 6.93 (d, $J = 8.7$ Hz, 2H), 6.73 (d, $J = 8.9$ Hz, 2H), 3.85 (s, 3H), 3.08 (s, 6H). m/z: calcd for $C_{18}H_{20}NO_2^+$[**1c** + H]$^+$: 282.1489, found: 282.1489.

2.2. Fabrication and measurement of the memory device

The indium–tin oxide (ITO)/glass were pre-cleaned with water, acetone, and alcohol in an ultrasonic bath for 20 min respectively. The film of **1a**–**c** (about 80 nm in thickness) was vacuum evaporated on indium–tin oxide (ITO) glass substrate at a pressure below 10^{-6} Torr. A layer of aluminum (about 100 nm in thickness) was thermally evaporated at a pressure below 10^{-6} Torr to form the top electrode. All electrical measurements of the devices were characterized under ambient conditions, without any encapsulation, using a HP4145B semiconductor parameter analyzer.

2.3. Measurement of electrical properties

The electrical properties of the devices were measured at room temperature under ambient conditions. The memory effects of **1a** and **1b** were demonstrated by the typical current density–voltage (J–V) curves for this sandwich device.

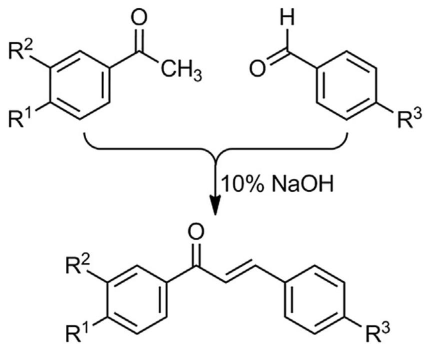
2.4. DFT calculation

The ground-state geometries of **1a** and **1b** were fully optimized using the density functional theory (DFT) with B3LYP/6-31G(d) method, and the optimized geometries at the excited state were studied at the CIS/6-31G level, as implemented in Gaussian software [24]. Following each optimization, the vibrational frequencies were calculated and the results showed that all optimized structures are stable geometric structures, based on which, molecular physical properties, such as Frontier Molecular Orbitals (FMOs), electrostatic potentials (ESPs), NBO charges and dipole moments, were given. To perform geometry optimizations in the presence of an electric field, a finite field was added to calculation in the x direction of molecules.

3. Results and discussion

3.1. Synthesis and preparation of device

The chalcone can be easily obtained by direct condensation between the aromatic aldehyde and the substituted acetophenone, using inorganic base as catalyst in ethanol. The pre-calculation results indicated that a negative ESP region locates at the oxygen atom in the α,β-unsaturated ketone of chalcone. So compounds **1a**–**c** (Scheme 1), which obtained by the simple Claisen–Schmidt condensation [25], were selected in this paper.



1a-c

1a: R^1= NO_2, R^2=H, R^3=OCH_3;
1b: R^1=H, R^2= NO_2, R^3=OCH_3;
1c: R^1=$N(CH_3)_2$, R^2=H, R^3=OCH_3.

Scheme 1. Synthesis of chalcone **1a**–**c**.