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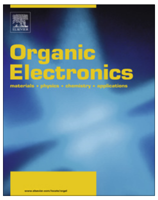

# A novel organic electrical memory device based on the metallofullerene-grafted polymer (Gd@$C_{82}$-PVK)

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## ABSTRACT

The ITO/Gd@$C_{82}$-PVK/Al sandwich nonvolatile memory device was developed based on polymer containing carbazole moieties as electron donors and Gd@$C_{82}$ as electron acceptors for the first time. The results of I–V characteristic test indicated that the new material exhibited typical bistable electrical switching and a nonvolatile rewritable memory effect, with a turn-on voltage of about $-1.5$ V and an ON/OFF-state current ratio of more than $10^4$. We propose that such a low turn-on voltage is caused due to the encaged metal and the DFT calculation indicated that the encaged metal served as an important electron trapping center, which facilitated the arrival of turn-on voltage.

## 1. Introduction

In the past decades, a large number of theoretical and experimental studies have demonstrated that carbon nano-materials, such as supramolecular fullerenes, one-dimensional nanotubes, and atom-thick graphene, are of great importance in a variety of new functional materials for electric, optoelectronic, and photonic devices [1–3]. The existence of a great *p*-conjugation system was the common feature for this kind of materials, thus they had good ability of accepting electron, which made them good application prospects in molecular electronic devices and other fields [4,5]. For example, the electron-transfer composite which formed with carbon nano-material as the acceptor and polymer as the donor material had WORM nature. Compared with inorganic storage materials, the organic memory materials have certain advantages in flexible, large area film-forming, low cost and so on [6–11]. Meanwhile, developing new materials with high read-write speed, low-power consumption, multi-value storage capacity and other excellent properties have been a subject for the study of next-generation non-volatile storage devices [12–15].

In recent years, the application of endohedral metallofullerenes (EMFs) in nuclear magnetic resonance contrast agents [16], biological tracer [17], photoelectric materials [18,19] and other fields had already been confirmed, which had become a hot research topic. It was of great significance to further expand the applications of EMFs by using their special advantages in structure [20,21] and properties [22]. However, due to the production limitation of EMFs, the research of metallofullerene polymer was rarely reported. In 2010, the first Gd@$C_{82}$-PS polymer was

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synthesized by our group [23]. It was found that the metallofullerenes had greater ability to capture free radicals, and the spectral properties, thermal stability and electrochemical properties of Gd@$C_{82}$-PS were also studied. Then, Gd@$C_{82}$ grafted poly(N-vinylcarbazole) (Gd@$C_{82}$-PVK) was successfully synthesized by free radical solution polymerization method [24].

Same as fullerenes, metallofullerenes had a highly three dimensional delocalized *p* electron conjugated structure, and could be used either as electron acceptor or as electron donor to form charge transfer compound with polymers containing electron withdrawing or electron donor compounds. The charge transfer was one of the reasons why certain materials had the flash storage performance. For instance, the electron affinity for $C_{60}$ [25] and Gd@$C_{82}$ [26] was proved to be 2.7 and 3.3 ± 0.1 eV, respectively. Therefore, the electron acceptance ability of metallofullerene was better than $C_{60}$. Furthermore, due to its larger carbon cage structures, the withdrawed electrons might delocalized effectively in the giant *p*-conjugation system of metallofullerene. Most importantly, the biggest difference between metallofullerene and fullerenes was the existence of the inner atom in metallofullerene, the electron of which could be transferred to the carbon cage of fullerenes and further affect its electron donor and withdraw ability.

Our current interest is to build the first metallofullerene-based memory device, and to study the roles of metals in the system. We have synthesized the Gd@$C_{82}$-PVK polymer by direct covalent attach between Gd@$C_{82}$ and poly(N-vinylcarbazole) (PVK) , and characterized its structure and properties by UV–Vis, FTIR, and XPS [24]. In this report, Gd@$C_{82}$-PVK was successfully applied in ITO/Gd@$C_{82}$-PVK/Al sandwich structures and the memory properties were evaluated. Furthermore, the theory calculation indicated that the encaged metal may serve as the important electron trapping center, *i.e.* the electrons move from VK group to the $C_{82}$ cage, and eventually to encaged gadolinium. This is the first example of a meatllofullerene-based memory device. PVK-Gd@$C_{82}$ is thus an example of a new type charge-transfer complex that integrates the conventional organic and inorganic charge transfer complexes.

## 2. Experimental and computation details

Gd-metallofullerene Gd@$C_{82}$ (99.5%) was produced and isolated with the industrial-scale production line of metallofullerenes firstly established in Institute of High Energy Physics. VK was bought from J&K Chemistry. The Gd@$C_{82}$-PVK polymer was synthesized and characterized according to Ref. [24].

### 2.1. Electric memory device

The memory properties of ITO/Gd@$C_{82}$-PVK/Al sandwich structures were evaluated. Before the fabrication of the Gd@$C_{82}$-PVK polymer layer, the ITO glass substrate was precleaned by ultrasonication with water, acetone, and ethanol for 15 min, respectively. A toluene solution of Gd@$C_{82}$-PVK (10 mg/ml) was spin-coated onto the ITO substrate under room temperature and the thickness of polymer layer was kept at about 50 nm. After removing the solvent, a 100 nm-thick Al top electrode was thermally evaporated through a shadow mask of $0.8 \times 0.8\ \mathrm{mm}^2$ in size. The current–voltage (I–V) characteristics were performed using a Keithley B1500 semiconductor parametric analyzer. All of the electronic measurements were performed in ambient conditions.

### 2.2. Computational methods

Geometry optimizations and electronic structure calculations for Gd@$C_{82}$, VK (one unit of PVK) and VK-Gd@$C_{82}$ (one unit of PVK-Gd@$C_{82}$) were performed by density function theory (DFT) using the Becke's three-parameter functional with the Lee, Yang, and Parr correlation functional method (B3LYP) [27]. The split-valence 6-31G(d) basis set [28] was used for nonmetals C, N and H. The scalar-relativistic effective core potentials (ECP) and basis set developed by Cundari and Stevens [29] were used for Gd, where the 46 inner electrons are replaced by the ECP and the outer 4f5s5p5d6s electrons are treated in the valence region. Previous experiments and theoretical calculations have shown that the ground-state geometry of Gd@$C_{82}$ has a $C_{2v}$ symmetry, with Gd atom located closely to the hexagonal ring along the $C_2$ axis [20,21]. At ground state, Gd@$C_{82}$ has a spin multiplicity of 7 ($M = 7$) [22]. Accordingly, the spin multiplicities were set to be 7 for Gd@$C_{82}$ and VK-Gd@$C_{82}$ in our calculations. The outer cage of Gd@$C_{82}$ has 35 symmetrically inequivalent C–C bonds, which are all possible to react with VK. To determine the energetically favorable reaction site, we calculated the relative stability for the 35 1, 2-hydirdes of Gd@$C_{82}$ (*i.e.*, Gd@$C_{82}H_2$). The hydrogenated C–C bond of Gd@$C_{82}H_2$ with the lowest energy was taken as the addition site for VK. All calculations were carried out using the Gaussian 09 program package.

## 3. Results and discussion

### 3.1. The electric memory device and its I–V characteristics

ITO/Gd@$C_{82}$-PVK/Al sandwich structure device was tested by using semiconductor parameter analyzer to record the current with voltage variation (Fig. 1).

The current–voltage (I–V) characteristics indicated that ITO/Gd@$C_{82}$-PVK/Al had the single pole resistance changing property (Fig. 2). Starting from the low conductivity state, the current density showed a tendency to increase when the applied negative voltage raised from 0 V to −2.0 V (with ITO as the anode and Al as the cathode, sweep 1). However, the current remained low until the turn-on voltage (−1.45 V) was reached. At this point, the current increased sharply, indicating device was transited from the low-conductivity state (OFF) to the high-conductivity state (ON), which was equivalent to the “writing” process in a digital memory cell. When it was swept from −2.0 V to 0 V (sweep 2), the current of the device was still at high value. This high-conductive state was kept in the