



Changing the stability of polymer-based memory devices in high conductivity state via tuning the red-ox property of Hemin



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ABSTRACT

Two polymer-Hemin composites, AB type block copolymer (PStCH-*b*-P4VP): Hemin and homopolymer of poly(4-vinylpyridine) (P4VP): Hemin, can be fabricated into sandwich memory devices. The memory device characteristics of the PStCH-*b*-P4VP: Hemin blends can show Flash memory behavior, while the P4VP polymer with Hemin only shows write-once-read-many-times (WORM) performance. Charge transfer and nanocomposite redox are probably responsible for the conductance-switching behavior. The results of cyclic voltammogram (CV) measurement indicate that the reversible Fe^{III}/Fe^{II} redox reaction is preserved well in the composite PStCH-*b*-P4VP: Hemin, while only polymer oxidation is observed in the P4VP: Hemin system. Due to the hindrance of StCH moiety, the coordination of pyridine and Fe^{II} can keep the Fe^{II} active. The P4VP has a more flexible chain that saturates the Fe^{II} center and results in stable coordination; Fe^{III}/Fe^{II} redox reaction is therefore an obstacle. By tuning the coordination surroundings of the metal ion, different memory types can be obtained.

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1. Introduction

Organic memories have recently received a tremendous amount of attention for application toward next-generation information storage [1–3]. Compared with inorganic silicon-based counterparts, organic and polymeric materials-based organic memory devices are advantageous due to their low-cost potential, flexibility, high-density data storage and miniaturization in size [4–9]. Furthermore, their potential for application towards synaptic mimicking and neuromorphic computing has cemented their place in the scientific spotlight.

Over the past decade, there have been quite a few reports of organic and polymeric materials containing coordination compounds being used to fabricate sandwich structured memory devices; these devices have reportedly exhibited good memory

performance [10–19]. Ma's group utilized lanthanide complex as active layer for 'write-read-erase' memory cycles through an OLED [20]. However, the problems of phase separation and ion aggregation must be considered, as they may cause uneven dispersion that is disadvantageous to memory performance. For the solution of this problem, Ree's group obtained a write-once-read-many-times (WORM) memory device based on nanoscale thin films of a soluble hyperbranched copper phthalocyanine (HCuPc) polymer [21]. One report originated from Cho's group, who demonstrated LBL (Layer-by-Layer) assembled ferritin multilayers that exhibited bistable electrical-switching behavior; using these devices, it was possible to create nonvolatile memory under applied voltages [22]. To address these issues in our study, we chose an appropriate coordination compound and a polymer with functional groups that reliable disperse through hydrogen bond and coordination bond.

Porphyrins and their derivatives are a kind of large π -conjugated molecules with good thermal stability [23,24]. The optical bandgaps and redox potentials of porphyrins can be tuned by metal insertion into the core and modification at the peripheral positions. Iron porphyrin-like compounds are very important in biological systems because they play a crucial role in the storage and

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transport of electrons and oxygen. Additionally, they are cheap organic semiconductor materials with the excellent photoelectric properties, widely used in organic solar cells and molecular optoelectronic devices [25–29]. It is particularly interesting to note that the Fe center in Hemin shows different redox capacities when located in distinct life systems. Furthermore, we choose two types of polymers, homopolymer poly-4-vinylpyridine (P4VP) and AB type block polymer with 4-vinylpyridine (4VP) block. We selected the 4VP as the second block and opportunely tune the 4VP block ratio in order to improve the diffusion and solubility of Hemin in the polymer DMF solution via coordination and hydrogen bond to investigate the redox capacity of iron in different coordination environments. The film of the PStCH-*b*-P4VP: Hemin and P4VP: Hemin composites were fabricated by spin coating. The device shows the Flash memory characteristic of the PStCH-*b*-P4VP: Hemin matrix, but write-once-read-many-times (WORM) memory characteristic of the P4VP: Hemin. Additionally, cyclic voltammogram (CV) measurements and conductive atomic force microscopy (C-AFM) were used to further demonstrate that the switching mechanism of the composites mainly originated from charge trapping and release within the redox sites of the Hemin. CV and C-AFM also showed that chalcone groups in block copolymers can serve as “obstacles” to block the aggregation of Hemin, providing an effective approach to optimize memory characteristics.

2. Experimental section

2.1. Materials

Potassium carbonate (K_2CO_3 , 99%), *N,N*-dimethylformamide and potassium hydroxide (KOH, 96%) were purchased from Shanghai Sinopharm. Hemin (95%) was ordered from TOKYO Chemical Industry (TCI). 4'-Hydroxyacetophenone (98%), 4-diethylaminobenzaldehyde (98%) were purchased from Aladdin. Cyclohexanone (Sinopharm Chemical Reagent, 96%) was purified by distillation. 4-Vinylbenzyl chloride (TCI, 90%) was obtained by column chromatography (aluminum oxide, neutral). AIBN was recrystallized from methanol before use. 4-vinylpyridine (Sinopharm Chemical Reagent, 96%) was obtained by column chromatography (aluminum oxide, basic). The poly(4-vinyl pyridine) (P4VP; $M_w = 16 \text{ kg mol}^{-1}$) was purchased from Sigma–Aldrich. All other reagents and solvents were used as received without further purification (see Fig. 1).

2.2. Instrumentation and characterizations

All of the device's electrical measurements were characterized under ambient conditions, without any encapsulation. ^1H NMR spectra were measured on an Inova 400 MHz FT-NMR Spectrometer. Elemental analysis was performed on an Italian 1106 FT analyzer. UV–visible absorption spectra were recorded by a Perkin-Elmer- λ -17 spectrophotometer at room temperature. The fluorescence spectra were measured on an Edinburgh-920 fluorescence spectra photometer (Edinburgh Co. UK). The weight-average (M_w), number average (M_n) molecular weight and polydispersity index (PDI) were determined by gel-permeation chromatography (GPC) on Waters1515 Gel Chromatograph with *N,N*-dimethylformamide (DMF) as an eluent. Thermogravimetric analysis (TGA) was conducted on a TA instrument Dynamic TGA 2950 at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ under a N_2 flow rate of 50 mL min^{-1} . Cyclic voltammetry (CV) measurements were carried out at room temperature using an ITO working electrode, a reference electrode Ag/AgCl, and a counter electrode (Pt wire) at a sweep rate of 20 mV s^{-1} (CorrTest CS Electrochemical Workstation analyzer) in a 0.1 M acetonitrile solution of tetrabutylammonium hexafluorophosphate (n -

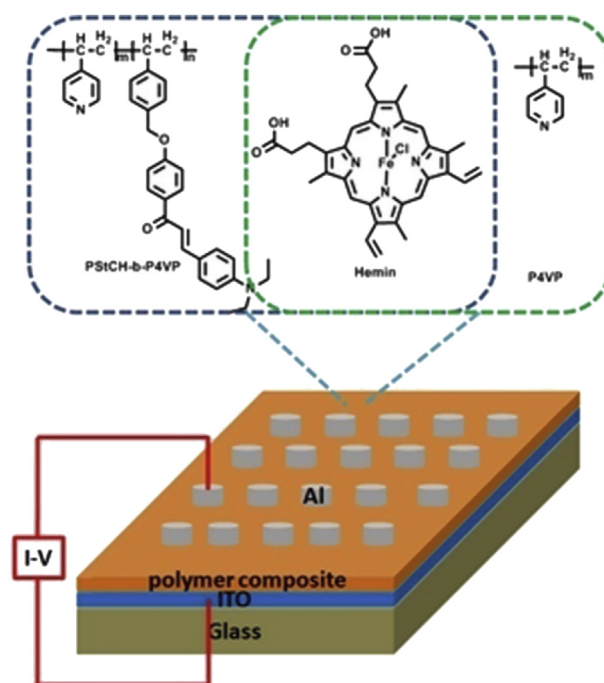


Fig. 1. The structures of polymers and polymer composites; the diagram of sandwiched memory device.

Bu_4NPF_6). Atomic force microscopy (AFM) measurements were performed by using an MFP-3DTM (Digital Instruments/Asylum Research) AFM instrument. Differential scanning calorimetry (DSC) analyses were performed on a Shimadzu DSC-60A Instrument. Fourier transform infrared (FT-IR) spectra of the polymers and composites were recorded on a Varian CP-3800 spectrometer in the range of $4000\text{--}400 \text{ cm}^{-1}$.

2.3. Synthesis of CPDN

2-cyanoprop-2-yl-1-dithionaphthalate (CPDN) was prepared according to previously reported procedures. ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.16 (m, 1H), 7.88 (m, 2H), 7.53 (m, 2H), 7.46 (m, 2H), 1.98 (s, 6H).

2.4. Synthesis of monomer and polymers

The monomer and polymers were synthesized as described in the references [30]. The number average molecule weights of homopolymer and block ratio of StCH to 4VP were tuned by controlling the reaction time and ratios of monomer to initiator or macroinitiator.

2.5. Device fabrication

The indium tin oxide (ITO) glass substrate was pre-cleaned sequentially with deionized water, acetone and alcohol for 20 min using an ultrasonic bath. PStCH-*b*-P4VP containing 0–7.5% Hemin (mass ratio of [Hemin]/[PStCH-*b*-P4VP]) were prepared in *N,N*-dimethylformamide and stirred for 1 h to form homogenous aging solutions. The solutions were filtered through micro filters with a pinhole size of $0.45 \mu\text{m}$, then spin-coated on a clean ITO glass substrate at a speed of 2000 rpm. The resulting film was annealed in a vacuum chamber at 10^{-1} Pa and $90 \text{ }^\circ\text{C}$ for 12 h. The thickness of organic layer was approximately 80 nm. Finally, the top metal electrode was obtained from an 80 nm-thick sheet of Al, which was

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