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High-performance non-volatile transistor memory devices using charge-transfer supramolecular electrets

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ABSTRACT

We demonstrated high performance non-volatile pentacene based OFET memory devices using charge-transfer (CT) supramolecules of poly(4-vinylpyridine) (P4VP) with two different chromophores, 3-(dicyanomethylidene)indan-1-one (1CN-IN) and 1,3-bis(dicyanomethylidene)indan (2CN-IN), respectively. The intermolecular CT interaction effectively introduced the chromophores as charge trapping sites into the P4VP matrix, leading to a controllable flash-type memory behavior. The electron-trapping ability of the supramolecular electrets was increased with enhancing the chromophore composition in the supramolecules. The experimental molar ratio x of chromophores binding to the repeating unit of P4VP, however, was limited to 0.30 for $P4VP(1CN\text{-}IN)_x$ or 0.45 for $P4VP(2CN\text{-}IN)_x$. The 2CN-IN with one more electron-withdrawing dicyanomethylene group, compared to 1CN-IN, provided a better electron-trapping ability and thus obtained a larger memory window. The device based on $P4VP(2CN\text{-}IN)_{0.30}$ electret exhibited the largest memory window (79 V) with the excellent retention ability of up to 10^7 s and endurance of over 100 cycles. The study revealed that the CT supramolecular electret could be as a facile and simple approach for future organic memory device applications.

1. Introduction

Organic non-volatile memory (ONVM) devices have received extensive research interest recently due to the advantages of low cost and easy processing for flexible electronic applications [1–5]. Among various memory device configurations (e.g. resistor- [6–8], capacitor- [2,3,9], and transistor-type [2,3,5]), organic field-effect transistor (OFET) memory is especially attractive because of its non-destructive readout operation, multiple-bit storage, and easy integration in a single transistor for a broad range of applications [2,3,5]. OFET memory structure is a conventional transistor with an additional charge storage layer (electret) inserted between the semiconductor layer and gate dielectric. Recently, various kinds of organic materials, including chargeable polymer electrets [10–13], ferroelectric oriented-dipole dielectric materials [14–15], nanoparticles (NPs) [16–18] and functional small molecules embedded gate dielectrics [19–21], were employed as a charge storage layer in OFET memories. Such material systems, however, usually required a complicated synthetic or hybridization procedure during the device fabrication. In addition, facing the scaling-down issue for future devices, the requirements of a high charge-storage capacity and a long retention are still a critical challenge.

Supramolecules are formed through complexation between an appropriate polymer matrix and a small molecule using non-covalent interactions, such as electrostatic interaction, hydrogen bonding, metal-ligand coordination, and charge transfer (CT). It allows one to generate functional nanocomposites via precisely controlling the spatial organization of small molecules at multiple length scales [19,22–31]. Indeed, the supramolceular approach provides an avenue to fabricate solution processable organic devices and integrate them into nanoscopic structures in thin-film electronics [19,22–29]. Recently, we reported hydrogen-bonded supramolecules consisting of sugar-based block copolymers and a amino functionalized pyrene, and discovered the tunable memory characteristics through the morphology attributed to the contact surface difference in the interlayer.[19] The optimized device using the supramolecular electret with the horizontal cylinder structure exhibited the excellent memory characteristics of a wide memory window of 52.7 V and a long retention time over 10^4 s. Similarly, the hydrogen-bonded composites of poly(4-vinylpyridine) based copolymers and hydroxyl-functionalized ferrocene [27] or conjugated small molecules [28] were used as the electrets and the good memory characteristics with an ON/OFF ratio up to 10^7 with an data endurance over 10^4 s were discovered [19,27,28]. Instead, CT complex could serve as the charge-storage sites in OFET memories because the partial charge transfer within the donor-acceptor moieties with an instant association and outstanding ability stabilized the charges [25,26]. However, the relationship between the CT supramolecular system and the OFET memory device characteristics has not been explored yet, to the best of our knowledge.

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In this study, we report the OFET memory properties of the supramolecular electrets prepared by attaching small chromophores, 3-(dicyanomethylidene)indan-1-one (1CN-IN) and 1,3-bis(dicyanomethylidene)indan (2CN-IN), to the P4VP via the intermolecular CT complexation between the lone pair of nitrogen in the pyridine group and the 2-methylidenepropanedinitrile group. P4VP and its copolymer have been commonly used as an electron donor for the supramolecular devices, since it possesses long pair electrons on the pyridine group, which can easily form a non-covalent bond (i.e. hydrogen bond) with an electron acceptor [19,27,28,32]. On the other hand, the indan-1,3-dione unit has a tunable electron-withdrawing ability through replacing one or both carbonyls by the dicyanomethylidene group [33,34]. Herein, we are especially interested in the multiple intermolecular charge-transfer interaction between P4VP and 2CN-IN or 1CN-IN. The prepared supramolecular composition was varied based on different molar ratio x of the chromophore to the repeating unit of P4VP (P4VP(chromophore)$_x$), where x ranges from 0 to 0.6 for investigating different CT efficiency on the OFET memory characteristics. The CT supramolecules were successfully and rapidly associated using a simple mixing method, which was confirmed by the UV–vis absorption spectra, Fourier transform infrared spectroscopy and atomic force microscopy. Moreover, the theoretical molecular conformations and the charge transfer states inside the supramoleculars were studied systematically. The pentacene based OFET memory device structure using the P4VP(chromophore)$_x$ charge storage layer is illustrated in Fig. 1. The effects of the charge-trapping ability, chromophore structure, and binding composition on the device characteristics were explored. Our study revealed that this simple supramolecular dielectric could be used to fabricate stable and premium ONVM device.

2. Experimental

2.1. Materials

Poly(4-vinylpyridine) (P4VP) homopolymer (M_w ~60,000 g mol^{-1}) and 1,3-bis(dicyanomethylidene)indan (2CN-IN) were purchased from Aldrich (St. Louis, MO). 3-(dicyanomethylidene)indan-1-one (1CN-IN) were obtained from Tokyo Chemical Industry Co. (Tokyo, Japan). Pentacene was purchased from Luminescence Technology Corp. (Hsinchu, Taiwan). All the chemicals were used as received and without further purification.

2.2. Preparation of P4VP(chromophore)$_x$ mixtures

The chromophores, 1CN-IN and 2CN-IN, were respectively incorporated with P4VP in solution to give the P4VP(chromophore)$_x$ mixtures for the formation of charge-transfer (CT) supramolecules. The homogeneous mixtures were obtained using the chloroform solvent after mechanical stirring for about 6 h at room temperature. P4VP(chromophore)$_x$ was prepared according to the chromophores with different molar ratio x of 0 to 0.6 to the repeating unit of P4VP, where the concentration of P4VP was fixed as 5 mg ml^{-1} in the solvent.

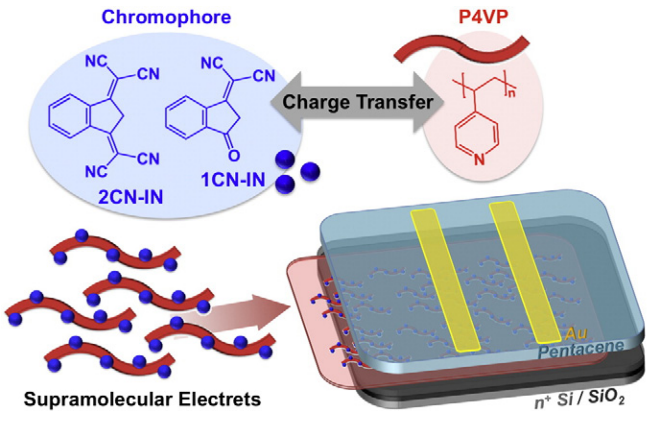

Fig. 1. Chemical structures of the studied supramolecules and the schematic configuration of pentacene-based OFET memory device.

2.3. Fabrication of the pentacene-based OFET memory devices

The transistor-type memory devices based on a pentacene thin film were fabricated on a wafer with a thermally grown 300-nm-thick SiO_2 dielectric on highly doped *n*-type Si as a gate electrode. The solution of P4VP(chromophore)$_x$ in chloroform was spin-coated at 1000 rpm for 60 s on a wafer and dried under vacuum (10^{-6} Torr) at room temperature for 1 h to remove residual solvents. The thickness of the prepared thin film was estimated to be 45–55 nm. A 50-nm-thick pentacene active layer was prepared by thermal deposition with a deposition rate of 0.3–0.4 Å s^{-1} at room temperature under 5×10^{-7} Torr. Note the deposition was preceded under room temperature in order to maintain the complexation of CT [26]. The top-contact source and drain electrodes were defined by the 80 nm-thick gold through a regular shadow mask, and the channel length (*L*) and width (*W*) were 50 and 1000 μm, respectively. The current-voltage (*I*–*V*) characteristics of the devices measured using a Keithley 4200-SCS semiconductor parameter analyzer in a N_2-filled glove box.

2.4. Characterization

UV–vis absorption spectrum was recorded using a Hitachi U-4100 spectrophotometer. For the measurement in the thin film state, the sample was diluted by chloroform to form 0.1 mg ml^{-1} of P4VP(chromophore)$_x$ solution and then spin-coated onto a quartz substrate. Infrared spectra were measured using a Bruker VECTOR22 FT-IR spectrometer at room temperature. Sample was prepared by casting one drop of the chloroform solution (~10 mg ml^{-1}) directly on potassium bromide substrate. Cyclic voltammetry (CV) was performed using a three-electrode cell in which ITO (the area of P4VP(chromophores)$_x$ film was about 0.5×1.5 cm^2) was used as a working electrode. A platinum wire was used as an auxiliary electrode, all cell potentials were taken using a Ag/AgCl, KCl (sat.) reference electrode. The electrochemical properties of the P4VP(chromophores)$_x$ films were detected under 0.1 M anhydrous acetonitrile solution containing tetrabutylammonium perchlorate (TBAP) as electrolyte. The thickness of the P4VP(chromophore)$_x$ film was measured with a microfigure measuring instrument (Surfcorder ET 3000, Kosaka Laboratory Ltd.). AFM image was obtained by using a NanoScope IIIa AFM (Digital Instrument) at room temperature. Commercial silicon cantilevers with typical spring constants of 21–78 Nm^{-1} was used to operate the AFM in tapping mode. Grazing Incidence X-ray Diffraction (GIXD) was conducted on beamline BL17A1 in the National Synchrotron Radiation Research Center (NSRRC), Taiwan. A monochromatic beam of $\lambda = 1.321$ Å was used. For the capacitance measurement, a metal-insulator-semiconductor (MIS) capacitor was fabricated by depositing gold electrodes on the polymer-coated *n*-type Si(100) wafers. The capacitance of the bilayer dielectrics was measured on the MIS structure using Keithley 4200-SCS equipped with a digital capacitance meter (model 4210-CVU).

2.5. Computational methodology

Theoretical molecular simulation of the P4VP(chromophore)$_x$ mixtures was calculated using the Gaussian 03 program package. Density functional theory (DFT) method, using Becke's three-parameter functional with the Lee, Yang, and Parr correlation functional method (B3LYP) with 6-31G(d) [35], was exploited for the optimization of ground-state molecular geometry, and electronic properties.

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