

Generating Digital Signals from Donor-Acceptor Block Copolymers

Structural characteristics of donor-acceptor polymers dominate the capability of data storage.

Memories of organic field-effect transistor (OFET) type have recently attracted extensive research interest for their use in wearable devices because of their structural flexibility, low cost and ease of processing. Based on an OFET architecture, polymer electret-based memory devices involve one charge-storage layer, prepared from polymer electrets, between the gate contact and the organic semiconductor channel (**Fig. 1(a)**).¹ Memory functionalities typically operate by electrical switching from trapped charges in the polymer electret upon applying programming or erasing the gate voltage. The charge-storage capability is hence extensively determined by the chemical nature of the polymer electrets.

Donor (D)-acceptor (A) polymers have been widely explored for OFET applications, because they can enhance the charge storage through an induced intramolecular charge transfer from the donor to the acceptor moiety under an applied electric field. It is generally accepted that the electrical properties of the fabricated OFET devices are critically dependent on nanostructured layers of polymer electrets. Understanding of the crystalline morphologies of D-A polymers and their correlations in the device performance would provide decisive notions to design new advanced OFET materials for memory devices. Grazing-incidence small-

and wide-angle X-ray scattering (GISAXS and GIWAXS) at **TLS 23A1** is able to capture the nanostructures of D-A polymers in the corresponding memory devices.

An international collaborative team led by Wen-Chang Chen (National Taiwan University) and Toshifumi Satoh (Hokkaido University) has reported a detailed study of transistor-type memory applications from a structural point of view of how the D-A block chain-length ratio of D-A blocks affects the performance of memory devices.² In their work, poly(3-hexylthiophene)-*block*-poly(pendent isoindigo) P3HT-*b*-Piso with varied chain length of Piso, a new D-A rod-coil block copolymer, was designed to be the charge-transporting and charge-storage layer for an OFET memory device. Distinct phase-separated P3HT (donor) and Piso (acceptor) domains respectively function as the hole-carrier transport and electron trapping, and efficiently prevent a charge recombination in the P3HT channels.

Growing fibrillar-like nanostructures with increasing coil length of the Piso block was revealed with an atomic-force microscope (AFM) and GISAXS (**Fig. 1(b)**). The orientation of molecular packing directly dominates the electrical properties of the D-A polymers. **Figure 1(c)** shows 2D GIWAXS patterns of P3HT-*b*-Piso thin films after annealing. Three diffraction signals at (100), (200) and (300) along the out-of-plane direction and the in-plane diffraction of (010) according to the π - π stack-

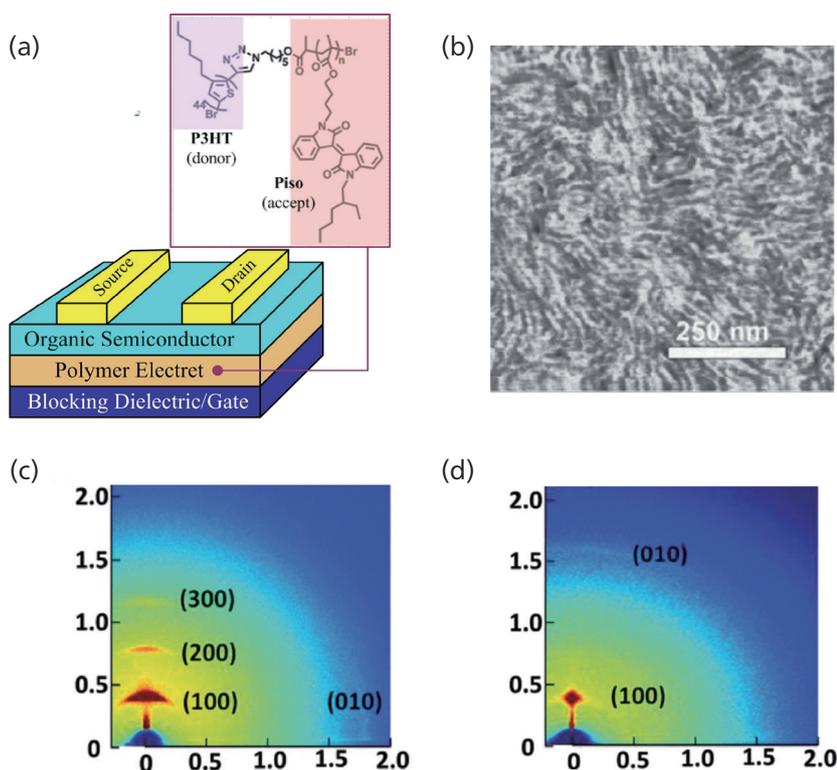


Fig. 1: (a) Schematic molecular structure of P3HT-*b*-Piso. (b) AFM image of P3HT₄₄-*b*-Piso₂₀. (c)-(d) 2D GIWAXS patterns of P3HT₄₄-*b*-Piso₂₀ and P3HT₄₄-*b*-Piso₁₀₀. [Reproduced from Ref. 2]

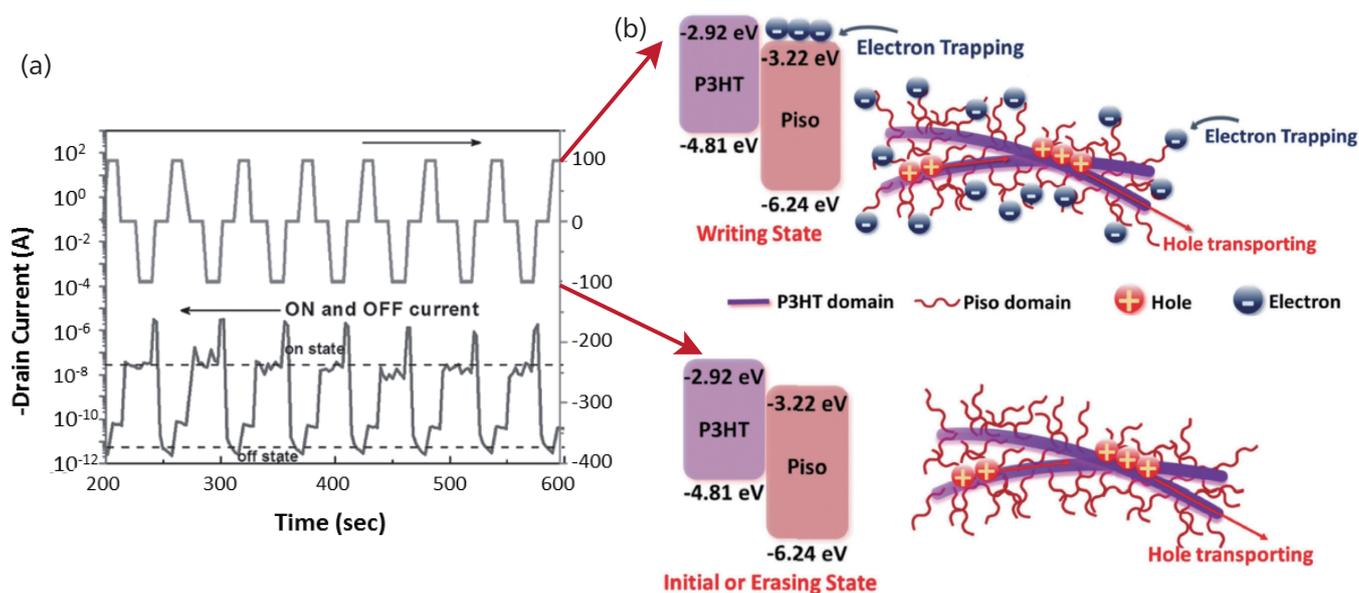


Fig. 2: (a) Reversible current response to a write-read-erase-read cycle of a P3HT₄₄-*b*-Piso₂₀ memory device. (b) Proposed mechanism of a P3HT-*b*-Piso memory device under a voltage bias and illustration of energy levels of P3HT rod and Piso coil. [Reproduced from Ref. 2]

ing indicate an edge-on packing orientation of P3HT crystals of the copolymers, but the edge-on orientation of P3HT crystals gradually alters to a flat-on orientation as the Piso block length is increased (**Fig. 1(d)**). This transition demonstrates that the Piso chain length can influence the orientation of molecular packing and even the charge-carrier transport.

From the memory characteristics of P3HT-*b*-Piso films with varied Piso chain length, the storage layer of the copolymer with a greater ratio of Piso block exhibited a large memory window but a poor field-effect mobility of the devices, because of the destroyed charge-transport network of P3HT domains with an increased Piso length. When the Piso length is small, the hole carrier can pass through a highly crystalline P3HT channel with an effective mobility; only few electrons can be trapped in the Piso domains, resulting in a poor stability of charge-storage retention. They found that P3HT₄₄-*b*-Piso₂₀ at an optimal D/A ratio features an appropriate memory window and a large mobility. **Figure 2(a)** shows the switching stability between ON/OFF states of a P3HT₄₄-*b*-Piso₂₀ device that was evaluated based on the measurement of a write-read-erase-read cycle. In **Fig. 2(b)**, during the writing, a positive electric field triggered many electrons at the level of the lowest unoccupied molecular orbital (LUMO) of Piso, leading to a positive threshold voltage (V_{th}) shift because the electrons generated in the Piso (acceptor) domains would induce extra holes that accumulated in the P3HT (donor) channels before scanning. In contrast, a negative voltage bias erased trapped electrons at the Piso domains; V_{th} then returned to the initial state. The results demonstrated that the device using the P3HT₄₄-*b*-Piso₂₀ electret

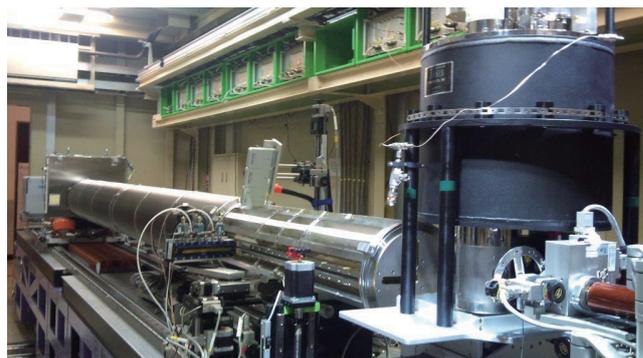
performed a memory (on/off) ratio about 10^5 over 100 cycles and has great potential for OFET memory applications.

This work significantly enhances our understanding of the mechanisms of these OFET memory devices using the new donor-acceptor P3HT-*b*-Piso block copolymer, advancing our knowledge about how the D/A ratio influences the hole mobility and electron affinity. Such findings enable us to design new device configurations for OFET memories. (Reported by Wei-Tsung Chuang)

This report features the work of Wen-Chang Chen, Toshifumi Satoh and their co-workers published in Adv. Funct. Mater. **26**, 2695 (2016).

TLS 23A1 IASW–Small/Wide Angle X-ray Scattering

- SAXS
- Materials Science, Thin Films, Soft Matter



A high-pressure/low-temperature (HPLT) system installed to the SWAXS endstation of TLS 23A1.

| References |

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Packing Principles for Donor-Acceptor Conjugated Molecules

Simple packing principles are found in lattices of structurally complicated D-A conjugated molecules.

Donor-acceptor (D-A) conjugated molecules have been the main character in the development of organic optoelectronics for the past 15 years. Above the length scale of a molecule, the solid-state morphology acts as an important intermedium to transfer molecular properties into useful device performance. Although synthetic chemistry of D-A molecules has been vigorously developed, the key factors that affect the assembly behavior and the lattice structures of D-A molecules have been only sparsely discussed.

D-A molecules require accessible thermodynamic and kinetic paths to assemble into an ordered solid-state structure. According to the Hunter-Sander principle, aromatic units in the edge-to-face or displaced face-to-face arrangements have favorable π - π interaction. As a result, conjugated molecules typically have a thermodynamic driving force to assemble into ordered phases. Nevertheless, D-A molecules are complicated in their chemical structures, because the molecules possess a (linear or curved) conjugated backbone, terminal substituents and lateral substituents. The easily distorted geometry of the conjugated backbone and the incommensurate packing dimensions of the back-

bone and the substituents make the assembled structure not only unpredictable but also kinetically difficult for the D-A molecules to assemble.

Chien-Lung Wang, Wei-Tsung Chuang and their colleagues at National Chiao Tung University and NSRRC, summarized more than 40 crystal lattices of conjugated oligomers to identify the packing principles for D-A conjugated molecules^{1,2}. By analyzing the packing models of the conjugated molecules in the crystal lattices, the morphological influences of the backbone curvature, terminal substituents and lateral substituents of D-A molecules were revealed as illustrated in **Fig. 1(a)**. Important packing models including a perpendicular arrangement and a tilted arrangement were identi-

fied from the lattices of the conjugated molecules with straight backbones, whereas scaly packing and intercalated packing were found in the lattices of those with curved backbones. In addition to the backbone curvature, terminal substituents were observed to influence the tilt angle of conjugated molecules in the plane of the tilted arrangement. Notably, because the lateral substituents prevent edge-to-face packing of the backbones, the (brick wall or staircase) face-to-face π -stacking was found in crystals of the laterally substituted conjugated molecules.

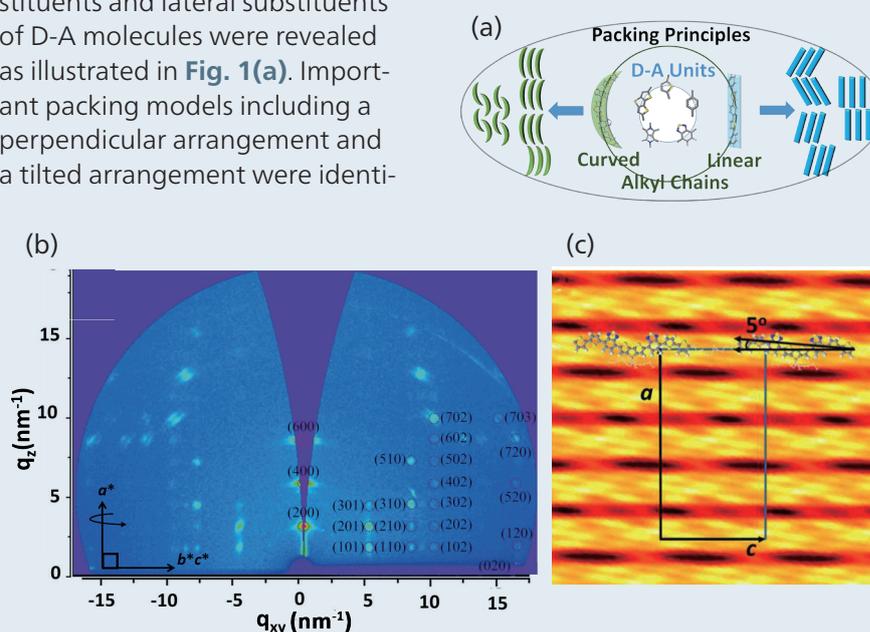


Fig. 1: (a) Packing principles of D-A conjugated molecules. (b) GI-XRD. (c) Electron density map of a DTS-F₂BT D-A molecule. [Reproduced from Ref. 1 and 2]