

Dithienylmaleimide-based D-A Conjugated Polymer Film: Photo-responsive Behavior and Application in Electrical Memory and Logic Gates

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Electronic Supplementary Information

Abstract Solid-stated smart polymers responsive to external stimuli have attracted much attention for potential application in the field of photoelectron devices, logic gates, sensor, data storage and security. However, it is a bigger challenge for polymers than that for small molecules in solid state to acquire stimuli-responsive properties, because polymers with high molecular weight are not as easy to change the packing structure as small molecules under external stimulation. Here, a D-A type alternating copolymer PTMF-o containing 3,4-bisthienylmaleimide (A unit) and fluorene (D unit) is designed and synthesized. Upon irradiation of sunlight, PTMF-o film exhibits a photo-response with the color altering from purple to colorless. It is attributed to the structure of copolymer transformed from ring-opening form (PTMF-o) to ring-closure form (PTMF-c), resulting from the oxidative photocyclization of 3,4-bisthienylmaleimide unit. Consequently, the ability of charge transfer (CT) from fluorene to 3,4-bisthienylmaleimide unit in PTMF-o can be easily weakened by light stimuli. PTMF-o film displays a WORM-type resistive storage performance for the strong CT. Interestingly, after exposure, the electrical memory behavior *in situ* transfers into FLASH type, due to weak CT in PTMF-c. PTMF-o film can also be employed as smart material to construct NAND and NOR logic gates by using light as input condition. The work provides a simple way to modify the electronic properties of polymers and realize stimuli-response in solid states.

Keywords Dithienylmaleimide; Photo-response; Electrical memory; Logic gate

Citation: Lv, W.; Wang, C.; Lin, X. C.; Mei, X. F.; Wang, W.; Yang, E.; Ling, Q. D.; Lin, Z. H. Dithienylmaleimide-based D-A conjugated polymer film: photo-responsive behavior and application in electrical memory and logic gates. *Chinese J. Polym. Sci.* 2021, 39, 1177–1184.

INTRODUCTION

Stimuli-responsive materials have received a growing concern and been applied in various fields, such as optical device, data memory, logic gate device, sensor, security application.^[1–5] Such materials are capable of variations in physical properties responding to external conditions.^[6–10] In general, the stimuli-responsive behavior is originated from the change of molecular or packing structure under external stimuli, which provides an effective method for modifying or modulating molecular properties, including polarity, electrochemical performance, optical refractive indices, magnetic response, electron conjugation, and so on.^[11–14] Compared with organic small molecule materials, polymers materials show many advantages: low cost, excellent scalability, film-forming ability, wearability and portability. Therefore, development of smart polymers is popular in the above various fields. Stimuli-responsive polymers

are prepared by the chemical polymerization of some specific monomers or the physical incorporation of the polymer and stimuli-responsive compound, which have been extensively investigated, responding to light, force, pH and temperature.^[15–19] In comparison with other stimulants, light is a clean, fast, safe and efficient stimulus with the ability of induction from outside the responsive system. The stimuli-responsive behaviors of these polymer are mostly carried out in solution state, which is not convenient in practical application and harmful to the operator. Due to their high molecular weight, however, polymers in solid are not as easy to change the molecular bonding and stacking structure as small molecules under external stimulation. Consequently, there are few reports on stimuli-responsive polymer films than those on small molecules. It is a huge challenge to develop such smart polymers, especially photo-responsive polymer films.

Diarylmaleimides have been used widely in the fields of organic optoelectronics and organic sensor, due to the simple synthesis, flexible modification, and tunable properties.^[20–28] Maleimide with two carbonyl groups shows the electron-withdrawing property. If its C(3) and C(4) positions are symmetrically substituted by electron-rich aryl groups, a pair of

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Received November 10, 2020; Accepted April 20, 2021; Published online June 15, 2021

cross-intercepted dipoles would be formed. Thus, electronic properties of diarylmaleimide could be adjusted by using different aryls, such as benzene, indole and thiophene. Interestingly, photophysical properties of 3,4-disubstituted arylmaleimide derivatives are sensitive to the external stimuli. In our previous researches, a series of diarylmaleimide derivatives exhibited stimuli-responsive properties upon the external stimuli of light, heat, pressure and solvent vapor.^[29–33] The interesting properties make it possible to construct stimuli-responsive polymer based on diarylmaleimide.

Here, we designed and synthesized a D-A (donor-acceptor) conjugated polymer (PTMF-o) containing fluorene units as donor and 3,4-dithienylmaleimide (DTM) units as acceptor. Under natural light, PTMF-o film shows color change from purple to colorless. Through the analysis of model compound and theory calculation, it was found that the photo-response of PTMF-o is derived from structure transform from the open form to the close one (PTMF-c) in the presence of visible light and oxygen (Scheme 1). As a result, the polymer film shows variable electrical memory behaviors from WORM (for PTMF-o) to FLASH (for PTMF-c). Additionally, two logic gates (NAND and NOR) have been constructed by making use of the light-stimulated response of PTMF-o film. The results provide a novel strategy for the development of diarylmaleimide-based multi-functional polymers, which can be used as smart materials in the stimuli responding field.

EXPERIMENTAL

Materials

All the reagents and solvents used in this study were purchased from Sinopharm Chemical Reagent Co., and used without further purification. Thin layer chromatography was performed on G254 silica gel plates of Qingdao Haiyang Chemical. Column chromatography was conducted on a Yantai Huanghai brand silica gel (200–300 mesh). The acceptor monomer (AM) and donor monomer (DM) were synthesized according to literature method.^[27]

Measurements

NMR spectra data were expressed in parts per million relative to the internal standard and were obtained on a BRUKER AVIII-400 NMR spectrometer. FTIR spectra data were measured by FTIR spectrometer (Nicolet 5700) by using the KBr pellets method. UV-Vis absorption spectra were obtained on a SHIMADZU UV-2600 spectrometer. Molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) analysis with polystyrene standard calibration (Waters high pressure GPC assembly model 1515 pump, refractive index detectors, solvent THF). Thermogravimetric analysis (TGA) was

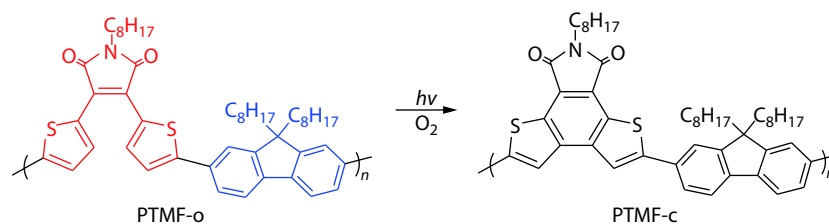
performed on a Mettler-Toledo 851e/822e analysis system under N₂ at a heating rate of 10 °C/min. Cyclic voltammetry (CV) measurements were conducted on a CHI600D electrochemical analyzer using a three-electrode cell under N₂ atmosphere. The polymer films on a glassy carbon electrode (working electrode) were scanned anodically and cathodically in a solution of tetrabutylammonium hexafluorophosphate (*n*-Bu₄NPF₆) in acetonitrile (0.1 mol/L) with Ag/AgCl and a platinum wire as the reference and counter electrode, respectively. The experiments were calibrated with the standard ferrocene/ferrocenium (FOC) redox system and assumption that the energy level of FOC is 4.8 eV below vacuum, and the value of 0.38 V was found for FOC versus Ag/AgCl. The energy levels of the highest occupied molecular orbital (HOMO) and the levels of lowest unoccupied molecular orbital (LUMO) of the polymers were calculated using the following equations: $E_{\text{HOMO}} = -(E_{\text{ox}}^{\text{onset}} + 4.42)$ eV, $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}^{\text{opt}}$, respectively, where $E_{\text{ox}}^{\text{onset}}$ was the onset potential for oxidation relative to the AgCl/Ag reference electrode, $E_{\text{g}}^{\text{opt}}$ was the optical band gap of the polymer. High resolution MALDI time of flight (TOF) mass spectra were obtained on a Bruker microflex LRF spectrometer.

Synthesis of the Polymer PTMF-o

Monomer AM (145.3 mg, 0.27 mmol), DM (180 mg, 0.28 mmol), [Pd(PPh₃)₄] (11 mg, 0.01 mmol) and toluene (3 mL), 2 mol/L aqueous solution of K₂CO₃ (1.3 mL) and TBAI (46 mg, 0.12 mmol) as phase transfer catalyst were added to a round-bottom flask. Under the protection of nitrogen, the mixture was vigorously stirred at 110 °C for 48 h. Bromobenzene (0.10 mL, 0.96 mmol) was dropped to react for 8 h and phenylboronic acid (0.11 g, 0.90 mmol) was added to end-cap the polymer for 8 h. After the mixture was cooled to room temperature, it was dropwise added to methanol. The fibrous solids were obtained by filtration. The solids were washed in a Soxhlet extractor with acetone for 1 day to remove oligomers and catalyst residues. The crude products were extracted by Soxhlet extractor with chloroform. The fractions in chloroform were concentrated under reduced pressure and precipitated into methanol. The resulting polymers were collected and dried under vacuum. Yield: 63%. ¹H-NMR (400 MHz, CDCl₃, δ, ppm): 8.01 (d, 2H), 7.72–7.65 (m, 6H), 7.45 (d, 2H), 3.67 (s, 2H), 2.04 (s, 4H), 1.71 (s, 2H), 1.28–1.06 (m, 34H), 0.88–0.77 (m, 9H). IR (cm⁻¹): ν 2930, 2848, 1696, 1530, 1410, 802. ¹³C-NMR (100 MHz, CDCl₃, δ, ppm): 170.58, 152.09, 150.80, 141.09, 132.73, 132.32, 129.23, 125.86, 125.22, 123.63, 120.47, 120.28, 55.56, 40.41, 38.80, 31.78, 29.98, 29.23, 28.56, 26.91, 23.82, 22.61, 14.09. GPC: M_n =14373, M_w =25590, PDI=1.78.

Synthesis of the Model Compound MC-o

AM (100 mg, 0.19 mmol), 9,9-dimethylfluorene-2-boronic acid pinacol ester (150 mg, 0.47 mmol), [Pd(PPh₃)₄] (11 mg, 0.01



Scheme 1 Photocyclization of PTMF-o in the presence of oxygen.

mmol) and toluene (3 mL), 2 mol·L⁻¹ aqueous solution of K₂CO₃ (1.3 mL) and TBAI (46 mg, 0.12 mmol) as phase transfer catalyst were added to a round-bottom flask. Under the protection of nitrogen, the mixture was vigorously stirred at 110 °C for 48 h. The crude products were purified by silica gel chromatography using petroleum ether. The resulting purple red products were collected and dried under vacuum. Yield: 70%. ¹H-NMR (400 MHz, CDCl₃, δ, ppm) 8.01 (d, 2H), 7.80–7.68 (m, 8H), 7.50–7.35 (m, 8H), 3.69 (t, 2H), 1.58–1.54 (br, 12H), 1.38–1.23 (m, 12H), 0.94–0.86 (m, 3H). ¹³C-NMR (100 MHz, CDCl₃, δ, ppm) 170.54, 154.53, 153.96, 150.61, 139.86, 138.48, 132.54, 129.10, 127.70, 127.17, 125.98, 125.24, 123.56, 122.70, 120.56, 120.36, 120.23, 47.03, 38.75, 31.83, 29.71, 29.19, 28.56, 27.16, 26.90, 22.67, 14.13. MALDI mass *m/z* [M⁺] Calcd. 757.305, Found 757.0930.

Photo-response Experimental Processes of PTMF-o and MC-o

The photo-response experiments were carried out in solution or thin solid film state of PTMF-o and MC-o under light irradiation. The light sources were obtained by a hand-held ultraviolet lamp with a radiant intensity of 3.46 W·sr⁻¹·m⁻² or a Keithley 2400 Source Meter under 100 mW/cm² illumination simulated AM 1.5 G irradiation with a radiant intensity of 43 W·sr⁻¹·m⁻². The concentration of solution was 1–2 mmol/mL. The thin solid film was prepared by drop casting or spin coating. The absorption spectra of irradiated PTMF-o indicate that PTMF-o has converted to PTMF-c almost completely. The crude products of MC-o under 365 nm light exposure were purified by column chromatography. The production (MC-c) yield is about 40%.

Fabrication and Characterization of Memory Devices

The memory devices were fabricated with the configuration of ITO/polymer/Al. The ITO-coated glass substrate was precleaned by ultrasonication with water, acetone, and isopropanol each for 20 min. The polymers were dissolved in chlorobenzene at a concentration of 10 mg/mL and spin-coated onto the ITO substrate at a speed of 1300 r/min for 60 s. The films thickness was about 45–50 nm measured by the Stylus Profilometer. Finally, Al top electrode with a thickness of 150 nm was deposited onto the polymer film surface through a shadow mask by thermal evaporation under vacuum. The electrical characterization of the memory devices was performed by a KEYSIGHT B1500A semiconductor device analyzer equipped with a KEYSIGHT 16440A SMU/Pulse generator on the SEMI-SHARE SM4 probe station.

Theoretical Calculations

All calculations were carried out with the Gaussian 09 package. Optimization of the geometry was performed by using B3LYP density functional theory (DFT). For all atoms, the 6-31G* basis set was used. The optical transitions were analyzed by time-

dependent DFT using the CAM-B3LYP/6-31* basis set.

RESULTS AND DISCUSSION

Design and Synthesis of PTMF-o

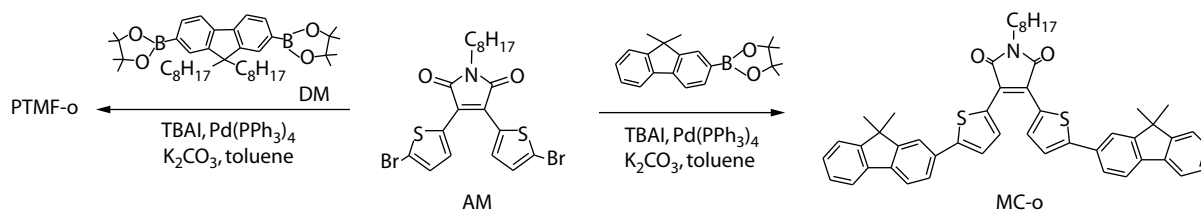
Dithienylmaleimide (DTM) and fluorene derivatives were chose as acceptor (A) and donor (D) unit, respectively, to prepare the D-A type copolymer PTMF-o. DTM was chosen as A unit for the photoactive feature of dithienyl maleic anhydride which can undergo an oxidative photocyclization under UV light through removing two H atoms at 3-position of thiophene.^[34,35] It means that the structure and electronic properties of PTMF-o can be altered by a light stimulus. Fluorene was selected as D unit for its good charge transporting ability.

The D-A type alternating copolymer PTMF-o was synthesized by Suzuki coupling reaction from DM containing fluorene and AM based on DTM in a moderate yield (Scheme 2). The same reaction was used to synthesize a model compound MC-o. The structure of PTMF-o and MC-o was determined by NMR and FTIR characterization. PTMF-o shows high molecular weight (*M_n*=1.43×10⁴), narrow polydispersity (PDI=1.78), and good solubility in chloroform, toluene and other common organic solvents. The excellent thermal stability of PTMF-o was revealed by thermogravimetric analysis (TGA) with 5% of weight loss at 390 °C (Fig. S1 in the electronic supplementary information, ESI). These results ensure that the polymer can be processed by solution method and applied in stable photoelectric devices.

Photo-response of PTMF-o

The absorption spectrum of PTMF-o in CHCl₃ was measured and shown in Fig. S2 (in ESI). The UV-Vis spectrum of PTMF-o is dominated by two main bands at around 362 and 568 nm. The former band can be attributed to the π-π* transition of fluorene group in the polymer, while the latter wide band should belong to the charge transfer (CT) from fluorene to DTM in the conjugated backbone. Interestingly, the intensity of the absorption band of PTMF-o at 568 nm gradually decreases, when irradiated under simulated sunlight or 365 nm of UV light (Fig. 1a and Fig. S3 in ESI), accompanied by solution color changing from purple to colorless. However, it takes a shorter time to complete the response process under sunlight than UV light. The different light-stimulated response time should be caused by the radiant intensity of light sources and the energy of light wave.

Compared with solution state, solid film material is more convenient to be used in practical application. Therefore, the photophysical property of PTMF-o in solid film was investigated. There are two main bands at about 364 and 565 nm in the absorption spectrum of PTMF-o in film, like in solution (Fig. S4 in ESI). Upon light irradiation, the film color of PTMF-o



Scheme 2 Synthetic route to PTMF-o and model compound MC-o.

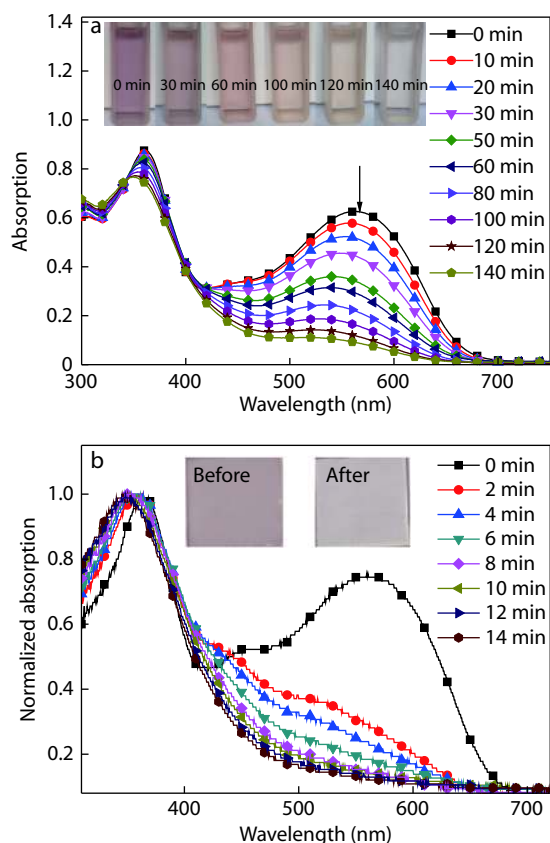


Fig. 1 Absorption spectra of PTMF-o in CHCl_3 solution (a) and film (b) irradiated by sunlight for different time.

also varies from purple to colorless (Fig. 1b inset). As shown in Fig. 1(b) and Fig. S5 (in ESI), the lower-energy absorption band drops gradually upon irradiation, and almost disappears after 12 min of sunlight irradiation or 50 min of UV light irradiation. In contrast to the absorption spectra in CHCl_3 solution, the spectra of PTMF-o in film show that a shorter time is needed to attain the same degree of changes. It should be contributed to different conformation of molecules in film and solution states. Closer packing of the polymer chains in film can induce more planar conformation of DTM, which favors ring-forming reaction. Above light exposure experiments were performed in air. In nitrogen, however, the absorption bands have no obvious variation after 40 min of irradiation under 365 nm UV light (Fig. S6 in ESI). The result reveals that oxygen played a key role in the photocyclization.

Possible Photo-responsive Mechanism

Based on the above experimental results, we speculate that the photo-responsive mechanism of PTMF-o is the photo-induced oxidative cyclization, which helps to remove two hydrogen atoms at 3-position of thiophene rings in the polymer, consequently leading to produce PTMF-c. Two thiophene rings are fixed in the backbone of PTMF-o, which is easy to undergo a photocyclization in oxygen under light irradiation to produce PTMF-c (Scheme 1). To verify the transforming process from PTMF-o to PTMF-c, $^1\text{H-NMR}$ spectra of the polymer were recorded before and after light irradiation (PTMF-o and PTMF-c) as shown in Fig. 2. After irradiation, the integral value of the

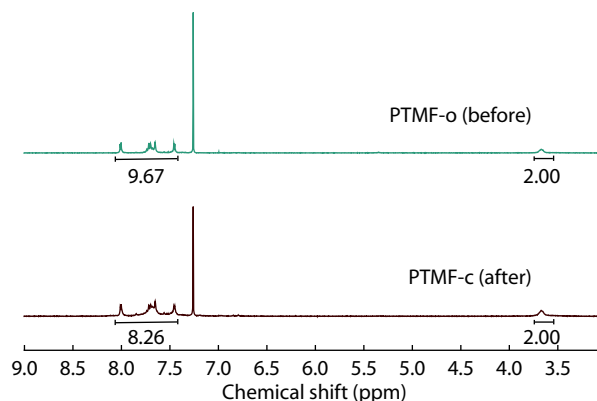


Fig. 2 Part $^1\text{H-NMR}$ spectra of polymer in d-CHCl_3 measured before and after light irradiation (PTMF-o and PTMF-c).

peaks at 7–8 ppm in $^1\text{H-NMR}$ spectra of polymer, corresponding to the number of aromatic protons, decreased from 10 to 8. It is well agreed with the structural feature of PTMF-o and PTMF-c. The photocyclization of PTMF-o can be done under mild air conditions without any catalysts, which is superior to the others requiring the participation of iodine or NBS, etc.^[36–38]

To further confirm the occurrence of oxidative photocyclization, the model compound MC-o with one DTM unit and two fluorene units was studied. The open-ring form (MC-o) was expected to turn into the close-ring form (MC-c) upon light-stimuli through two steps: photoisomerization and dehydrogenation. The first step is reversible, while the second one is irreversible (Scheme S1 in ESI). Indeed, the intensity of the absorption band at 570 nm of MC-o in solution gradually decreases with its color changing from purple red to colorless, under 365 nm of UV light (Fig. S7 in ESI). $^1\text{H-NMR}$ spectra of MC-o were measured before and after light irradiation (Fig. S8 in ESI). After irradiation, the integral value of the peaks at 7–8 ppm in $^1\text{H-NMR}$ spectrum of MC-o, corresponding to the number of aromatic protons, decreased from 18 to 16. The peak of the chemical shift 8.0 ppm assigning to the hydrogens in the thiophene rings disappeared, and other peaks were shifted after irradiation. Fig. 3 exhibits the $^1\text{H-}^1\text{H}$ COSY spectra of MC-o in d-CHCl_3 before and after light irradiation. Before light irradiation, the 2D NMR spectrum shows the cross peaks at 8.0 and 7.4 ppm in the low field range, caused by the proximity interaction of adjacent hydrogen in the thiophene rings. After light irradiation, the oxidative photocyclization led to the loss of the hydrogens in the thiophene rings ($\delta=8.0$ ppm). So, the cross peaks at 8.0 and 7.4 ppm disappear, corresponding to the close-ring form structure of MC-c. The MALDI mass spectra of MC-o and MC-c are shown in Fig. S9 (in ESI). The 757 value and 755 value in Fig. S9 (in ESI) are consistent with the described structure formulas of MC-o and MC-c. The difference of MALDI mass spectra is due to the two losing hydrogens in the thiophene rings after photocyclization. These results affirm the structural feature of MC-o and MC-c.

The absorption spectra of MC-o film in air and N_2 were shown in Fig. 4. The intensity of the absorption band of MC-o at 550 nm gradually decreases in air (Fig. 4a), while the intens-

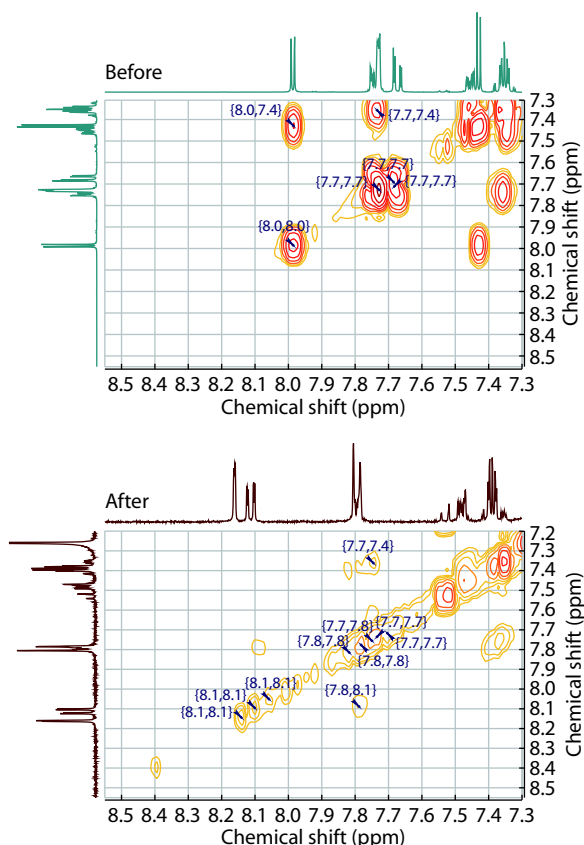


Fig. 3 ^1H - ^1H COSY spectra of MC-o in d-CHCl_3 measured before and after light irradiation.

ity of the same absorption band was almost in a constant level in N_2 (Fig. 4b). By light irradiation, the color of the MC-o film gradually changed from purple red to colorless in air, while kept unchanged in N_2 . The different results in air and N_2 are consistent with those of PTMF-o.

Theory Calculation

The electronic properties of PTMF-o before and after cyclization were analyzed by means of theory calculations. Fig. S10 (in ESI) shows the structure of the repeating unit (2M3F) of polymer PTMF-o including two DTM and three fluorene units. Open-ring form (2M3F-o) is expected to transfer into the close-ring form (2M3F-c) under irradiation. From calculated frontier orbital distribution and excited energy levels (Fig. 5), it is found that the HOMO of 2M3F-o mainly locates on the centre fluorene (D unit), while the LUMO is mainly distributed in two DTMs (A unit). However, the electrons in HOMO and LUMO of 2M3F-c extend to the whole molecule. It indicates that 2M3F-c has weaker CT interaction than 2M3F-o, resulting in larger bandgap of 2M3F-c (2.79 eV) than 2M3F-o (2.15 eV). Simulated absorption spectra (Fig. S10 in ESI) represent a blue shifting band from 2M3F-o to 2M3F-c. The electrostatic potential (ESP) of the molecule can partly represent the degree of the charge transfer interaction. As shown in Fig. S11 (in ESI), the ESP of repeating units in PTMF-o displays the obviously strong charge transfer interaction, while the ESP of repeating units in PTMF-c shows the relatively weaker and moderate charge transfer interaction. The calculated results are in agreement with the experimental data, indicating the

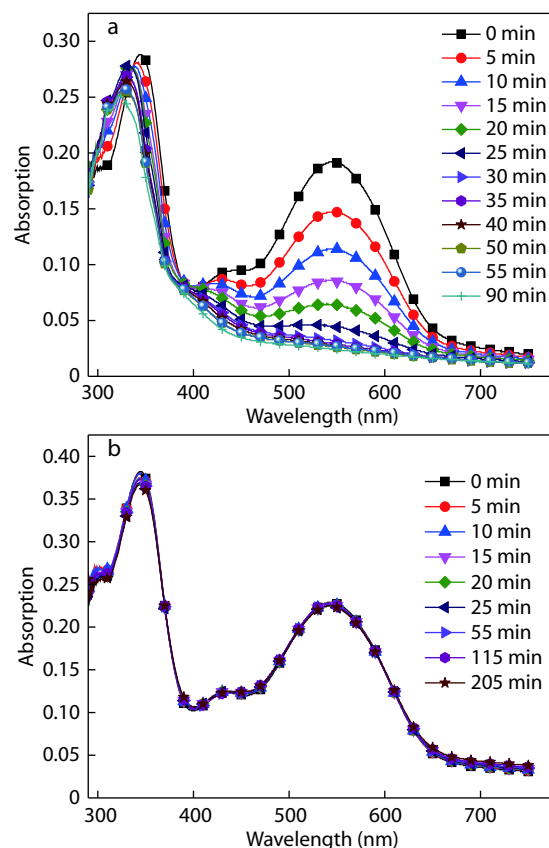


Fig. 4 Absorption spectra of MC-o film irradiated by 365 nm of UV light in air (a) in N_2 (b) for different time.

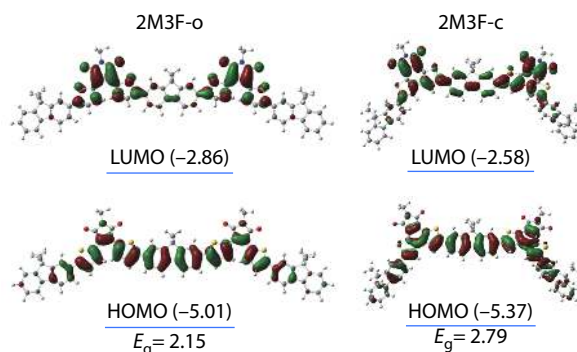


Fig. 5 Calculated frontier orbitals of 2M3F before and after cyclization.

occurrence of oxidative cyclization which can significantly affect the electronic property of the main chain in PTMF-o.

Electrochemical Properties of PTMF-o and PTMF-c

CV analysis was used to study the electrochemical behavior of PTMF-o and PTMF-c, and to estimate the HOMO and LUMO energy levels. The difference of the molecular structures should influence the HOMO and LUMO energy levels of the material. The optical band gaps (E_g^{opt}) of PTMF-o and PTMF-c were estimated from their film absorption edges as 1.79 and 2.14 eV, respectively. From the CV curves of PTMF-o and PTMF-c (Fig. S12a in ESI), it is found that the onset oxidation potentials of PTMF-o and PTMF-c were +1.05 V and +1.19 V, respectively.

Based on the onset potentials, the HOMO energy levels of PTMF-o and PTMF-c were calculated to be -5.47 and -5.61 eV, respectively, and the LUMO energy levels of PTMF-o (-3.68 eV) and PTMF-c (-3.47 eV) were obtained from the formula $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}^{\text{opt}}$. Fig. S12(b) (in ESI) shows the HOMO and LUMO energy levels for PTMF-o and PTMF-c along with the work functions of the electrodes. Under light irradiation, the optical band gap increased, the HOMO energy levels decreased and the LUMO energy levels increased, consistent with the previous theoretical calculation analysis. Furthermore, the change of material in electrochemical properties might obtain lower current value at the initial stage of applying the electric field, and lead to better resistance switching performance of the memory device.

Resistance Switching Performance

The ability of charge transfer (CT) between the donor and acceptor imposes an obvious effect on the electronic properties of polymers. The different structures and electrochemical properties of PTMF-o and PTMF-c have also adjusted the resistance switching performance of the materials.

Resistance switching behaviors of the polymer were demonstrated by the I - V characteristics of ITO/polymer/Al device in air. The I - V curves of the devices based on polymer film are shown in Fig. 6. In the case of PTMF-o (Fig. 6a), the device lies in the low conductivity state (OFF state) in the first sweep before $+2.96$ V of voltage. After that, the current level undergoes an abrupt increase, which indicates that the device

transfers from OFF state to ON state (sweep 1). The device keeps in the ON state for the subsequent sweep both positive and negative (sweep 2, 3, 4). Thus, the device can be used as a WORM device. Interestingly, the I - V curves of PTMF-c device (after irradiation) exhibit rewritable Flash memory behaviors (Fig. 6b). The device is in the low conductivity state initially in the first sweep under the positive voltage. Then, a sharp increase of the injection current occurs at $+0.93$ V, indicating a transition from OFF state to ON state (sweep 1). The current ratio between the OFF and ON state is 10^3 , which is essential for the memory device to work with the minimum misreading error. The device lies in the ON state for the following positive sweep (sweep 2). Meanwhile, the OFF state can be recovered by the reverse voltage at -2.79 V (sweep 3), which is equivalent to the erasing process of the device. The device keeps in the OFF state for the subsequent negative sweep (sweep 4). Both of the ON and OFF states of the device can be retained even after turning off the power, indicating the nonvolatile nature of the resistance switching effect. It is worth noting that the rewritable behaviors of the device are repeatable with high accuracy (sweep 5–8). The changes of the threshold voltages might be related to the dielectric relaxation of the polymer chain structure.^[39]

The long-term stability and the stimulus effect of the ITO/PTMF-c/Al device were evaluated from the retention time and stress tests of both the ON and OFF states (Figs. S13a and S13b in ESI). The results suggest that the resistance switching device possessed excellent reproducibility and high stability.

By applying an external electric field, electric charge carriers can move along the D-A polymer backbone for the CT transition from the donor to the acceptor, resulting in a sharp increase of the conductivity. The extent of charge transfer would significantly affect the performance of the devices. Too strong CT interaction easily forms a high conductivity state, while too weak interaction between the donor and acceptor keeps materials in the OFF state. Neither of them can realize the electronic bistability state (ON/OFF) of the devices. However, the structural variation affects the degree of CT. The stronger CT interaction of PTMF-o is responsible for its WORM memory feature, while the weaker charge transfer interaction of PTMF-c leads to Flash memory property. As a result, the WORM memory based on PTMF-o can be activated again by illumination, and turned into erasable FLASH memory. It is very useful to recycle and reuse Non-erasable WORM memory device.

Logic Gate Application

Recently, stimuli-responsive materials have shown huge potential in the applications of molecular logic system.^[40] However, most of these materials were used in solution state, and different chemicals were chosen as input conditions, which bring inconvenience and danger in the actual device operation. Solid-state materials,^[30] especially films, as well as photo as inputs,^[41] are popular to mimic logic operation. Based on the above results of multiple-stimuli response, two kinds of logic gates (NAND and NOR) could be constructed by using the PTMF-o film. Firstly, illumination and oxygen are selected as the two inputs, and the absorption intensity at 570 nm (I_{570}) as the output. The absorption spectra of PTMF-o film at different input conditions are shown Fig. S14(a) (in ESI). The absorption intensity of 0.5 is set as threshold value. Only the fourth input

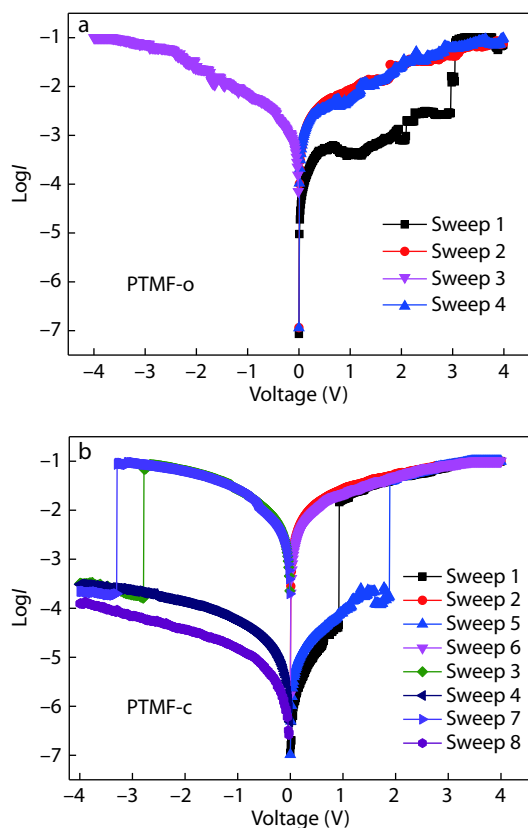


Fig. 6 Current-voltage (I - V) characteristics of the devices based on PTMF-o (a) and PTMF-c (b).

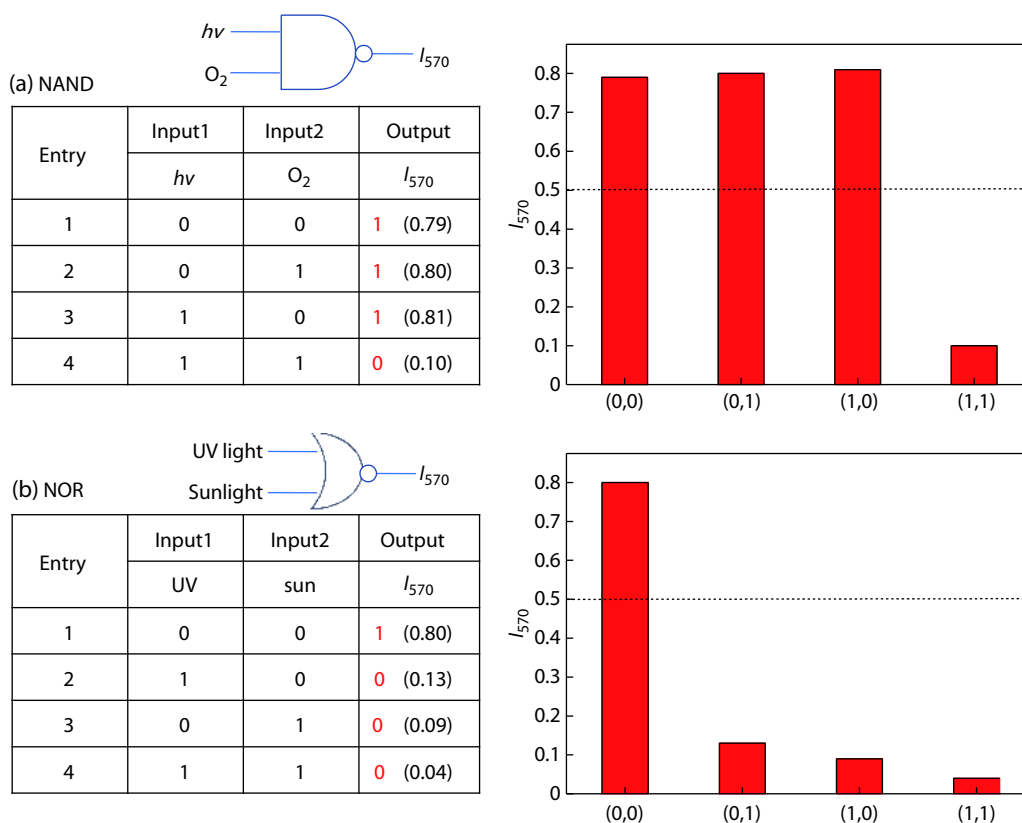


Fig. 7 True table of the NAND (a) and NOR (b) logic gates and the absorption intensity at 570 nm (threshold value of $I=0.5$).

condition (1, 1), namely illumination under oxygen, gives a weak absorption at 570 nm ('0' state), while other input conditions locate at '1' state. Consequently, a NAND logic gate is obtained (Fig. 7a). Secondly, when utilizing UV light and sunlight illumination as two inputs and the absorption intensity at 570 nm (I_{570}) as the output, a NOR logic gate can be available (Fig. 7b). From Fig. S14(b) (in ESI), it can be observed that only the condition without two inputs (0, 0) results in I_{570} more than 0.5 ('1' state), while other conditions are at '0' state.

CONCLUSIONS

In summary, a D-A type conjugated polymer PTMF-o has been obtained by employing fluorene as the donor and DTM as the acceptor. Two thiophene rings of DTM are fixed in the backbone of PTMF-o, forming relatively planar conformation which can make the structure of the polymer change from open-ring form (PTMF-o) into close-ring form (PTMF-c) under irradiation of sunlight. Therefore, the electronic property of polymer determined by the extent of CT from the donor to the acceptor is changed by light stimuli. The resistive switching device based on PTMF-o with the configuration of ITO/PTMF-o/Al was fabricated by spin-coating process. The memory devices show light-stimulated response behavior, altering from WORM (PTMF-o) to FLASH (PTMF-c). PTMF-o film can also be used as smart material to construct NAND and NOR logic gates. This work offers a simple and effective strategy on regulating photoelectric property of materials by external stimuli, replacing complex structural modification.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-021-2594-z>.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 22075044 and 21574021), the Natural Science Foundation of Fujian Province (No. 2018J01670), Educational Commission of Fujian Province (No. JAT170129), and the Scientific Research Starting Foundation for researchers with PhD of Fujian Normal University.

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