

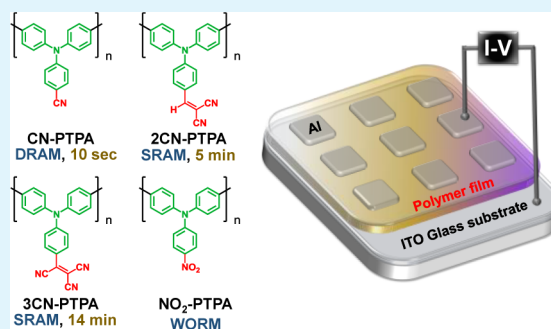
Substituent and Charge Transfer Effects on Memory Behavior of the Ambipolar Poly(triphenylamine)s

Jia-Hao Wu and Guey-Sheng Liou*

Functional Polymeric Materials Laboratory, Institute of Polymer Science and Engineering, National Taiwan University, 1 Roosevelt Road, 4th Sec., Taipei 10617, Taiwan

Supporting Information

ABSTRACT: A series of poly(triphenylamine)s (CN-PTPA, 2CN-PTPA, 3CN-PTPA, and NO₂-PTPA) with pendent acceptors (cyano, dicyanovinyl, tricyanovinyl, and nitro) have been readily synthesized by oxidative coupling polymerization using FeCl₃ as oxidant. The tunable memory properties of the ITO/polymer/Al sandwiched memory devices including DRAM, SRAM, and WORM could be achieved by introducing substituent acceptors with different extent of electronic delocalization and electron-withdrawing intensity into the poly(triphenylamine)s. The highly fluorescent CN-PTPA exhibited volatile DRAM memory characteristic due to the large band gap and weak intramolecular charge transfer capability. 2CN-PTPA and 3CN-PTPA showed volatile SRAM memory property with retention time of 5 and 14 min, respectively, depending on electron-withdrawing capability of the acceptors. Furthermore, NO₂-PTPA afforded nonvolatile WORM memory behavior attributed to the charge could be trapped into the nonconjugated nitro group even though the dipole moment and electron-withdrawing capability of nitro group were weaker than cyanovinyl groups. Moreover, except NO₂-PTPA, all the devices derived from cyano-containing ambipolar polymers including CN-PTPA, 2CN-PTPA, and 3CN-PTPA could be switched to the ON state and exhibited WORM memory behavior in positive unipolar *I*-*V* switching. This phenomenon indicated that the Al atoms preferentially interact with poly(triphenylamine)s containing cyano than nitro substituents.



KEYWORDS: triphenylamine, memory device, donor–acceptor, charge transfer, ambipolar

1. INTRODUCTION

Nowadays, the development of superior electronic devices, such as mobile phones and wearable devices, trend to miniaturization for high portability and data storage, which are important issues in the information technology (IT) industry. Recently, polymeric memory materials have attracted increasing attention for storage applications due to their rich structural flexibility, low-cost, solution processability, large area fabrication, and three-dimensional stacking capability¹ and could be expected to supplement conventional memory devices derived from Si-based integrated circuits. Resistive memory devices store information in the form of high (ON) and low (OFF) current states between the changes in the conductivities of the active materials at different electric fields. The donor–acceptor effect is an important mechanism for differentiating and explaining the memory behavior. A charge transfer (CT) complex is defined as an electron donor–electron acceptor (D–A) complex, characterized by electronic transition from ground state to excited state in which inter- or intramolecular electron transfer from the donor to the acceptor moieties could be produced under electrical bias, resulting in a sharp current increase as a highly conductive state. The D–A polymer system for the volatile and nonvolatile memory devices, including conjugated polymers,^{2–4} functional polyimides,^{5–7} nonconju-

gated polymers with pendant electroactive chromophores,^{8–10} and polymer hybrids^{11–14} were reported for obtaining electrical switching memory behavior.

Triphenylamine (TPA) derivatives and TPA-based polymers are well-known candidates for hole-transporting materials in organic optoelectronic devices, such as OLEDs, solar cells, and Li-ion batteries due to lower ionization energy and high hole-mobility of the resulting stable radical cation.¹⁵ Besides, the enhanced thermal stability and the glass transition temperature (*T*_g) could be expected by introducing of TPA units into the polymers because of its high aromatic content. Recently, some TPA-based organic molecules^{16–20} and polymers^{21,22} have been synthesized and investigated as resistive memory devices. For polymer system, the vinylene-based conjugated polymers having different backbone donors and the same side chain acceptor were prepared by Chen et al.,²¹ which TPA-based polymer showed nonvolatile write once read many (WORM) memory behaviors. Recently, novel thermally stable and electron-donating poly(triphenylamine)s (PTPAs) with pendant anthraquinone (AQ) electron acceptors were synthesized

Received: May 13, 2015

Accepted: July 2, 2015

Published: July 2, 2015

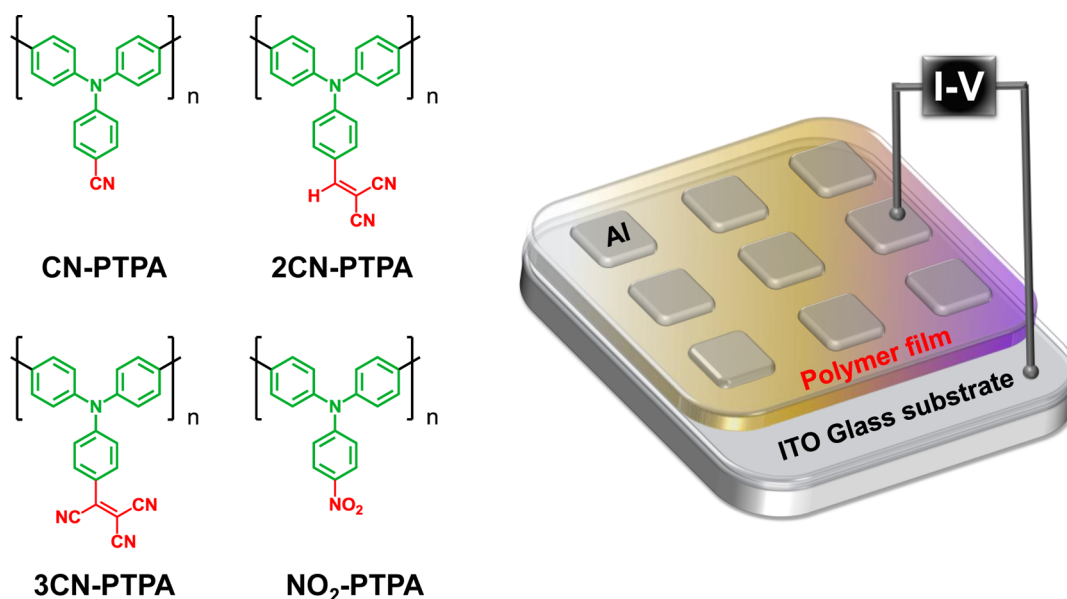


Figure 1. Chemical structures of PTPAs and the schematic diagram of the memory device consisting of a polymeric active layer sandwiched between an ITO bottom electrode and an Al top electrode.

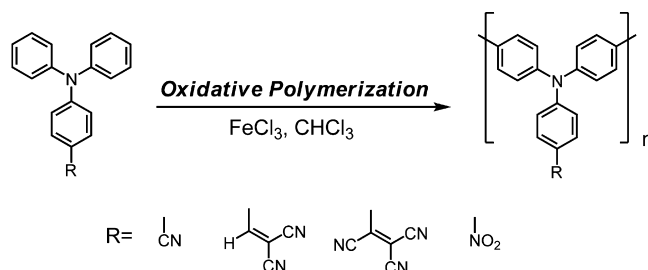
by our group for investigating the side-chain and linkage-mediated effects on the memory behavior. By incorporating an isolated ether group between the TPA donor and pendant AQ acceptor, the PTPA-OAQ based memory device revealed longer retention time in the ON state as opposed to PTPA-AQ.²²

To better understand the D–A system, we synthesized a series of poly(triphenylamine)s consisting of intrinsic electron-donating TPA main chain and different pendant substituent acceptors to investigate the inducing charge transfer effect on memory behavior of the obtained resistive polymeric memory devices (Figure 1). The CN-PTPA with high photoluminescence quantum yield (PLQY)^{23,24} implies lower intra- or intermolecular CT capability, and 2CN-PTPA and 3CN-PTPA contain dicyanovinyl and tricyanovinyl pendant substituents, revealing enhanced interaction of CT and much lower photoluminescence efficiency were synthesized, respectively. These two kinds of cyanovinyl pendant groups with higher extent of π -electron delocalization due to C–C double bond exhibit the influence and also play an important role on retention time of the resulting memory devices. In addition, NO₂-PTPA²⁴ with nitro substituent acceptor was also used to compare and demonstrate the electron-withdrawing capability and extent of electron delocalization of nitro pendant group, which is mostly confined within the nitro group itself. Furthermore, NO₂-PTPA with higher molecule weight (NO₂-PTPA-H) was also prepared to confirm the molecule weight effect on the memory behavior.

2. RESULTS AND DISCUSSION

2.1. Basic Characterization of PTPAs. Two novel PTPAs, 2CN-PTPA and 3CN-PTPA, were readily synthesized via oxidative coupling polymerization using FeCl₃ as oxidant (Scheme 1), and the detailed synthetic procedures are described in the Supporting Information. All resulting products exhibited enough molecular weight to afford thin films by spin-coating. The yield, molecular weights (Mw), and polydispersity (PDI) of the resulting polymers are summarized in Table S1 (SI). The Mw and PDI of cyano-based PTPA were around

Scheme 1. Synthesis Route of PTPAs



21 000–64 000 and 2.30–3.93, respectively. The nitro-based PTPA (NO₂-PTPA) was prepared with the Mw of 3000 and PDI of 1.15, while NO₂-PTPA-H, which revealed higher Mw of 76 000 and PDI of 4.84, was also synthesized to investigate molecular weight effect on memory behavior. The formation of PTPAs was confirmed by FTIR spectroscopy (Figure S4, SI) and ¹H NMR (Figure S5, SI). FTIR spectra show characteristic absorption bands at around 2217–2222 cm⁻¹ (CN) for cyano-based PTPAs, and 1583 and 1317 cm⁻¹ (NO₂) for NO₂-PTPA. In ¹H NMR spectra, the reacting site of 2CN-PTPA and 3CN-PTPA could be at *para*- and *ortho*- position during oxidative coupling polymerization (*para*-: 64% and *ortho*-: 36% for 2CN-PTPA; *para*-: 78% and *ortho*-: 22% for 3CN-PTPA). Because dicyanovinyl and tricyanovinyl group were very strong, electron-withdrawing moiety enhanced not only the reactivity resulting in higher molecular weight but also the reactivity of TPA cation radical at *ortho*- position.

The solubility test of the obtained polymers was measured qualitatively, and the results are summarized in Table S2 (SI). 2CN-PTPA and 3CN-PTPA with more bulky pendant groups could dissolve in the most of solvents and reveal better solubility than that of CN-PTPA. NO₂-PTPA also revealed good solubility comparing with NO₂-PTPA-H, which only could dissolve partially in high polarity solvent such as *N*-methyl-2-pyrrolidinone (NMP) ascribed to the highly chain packing and enhanced intermolecular interaction reported in our pervious report.²⁴ Thus, the low boiling temperature

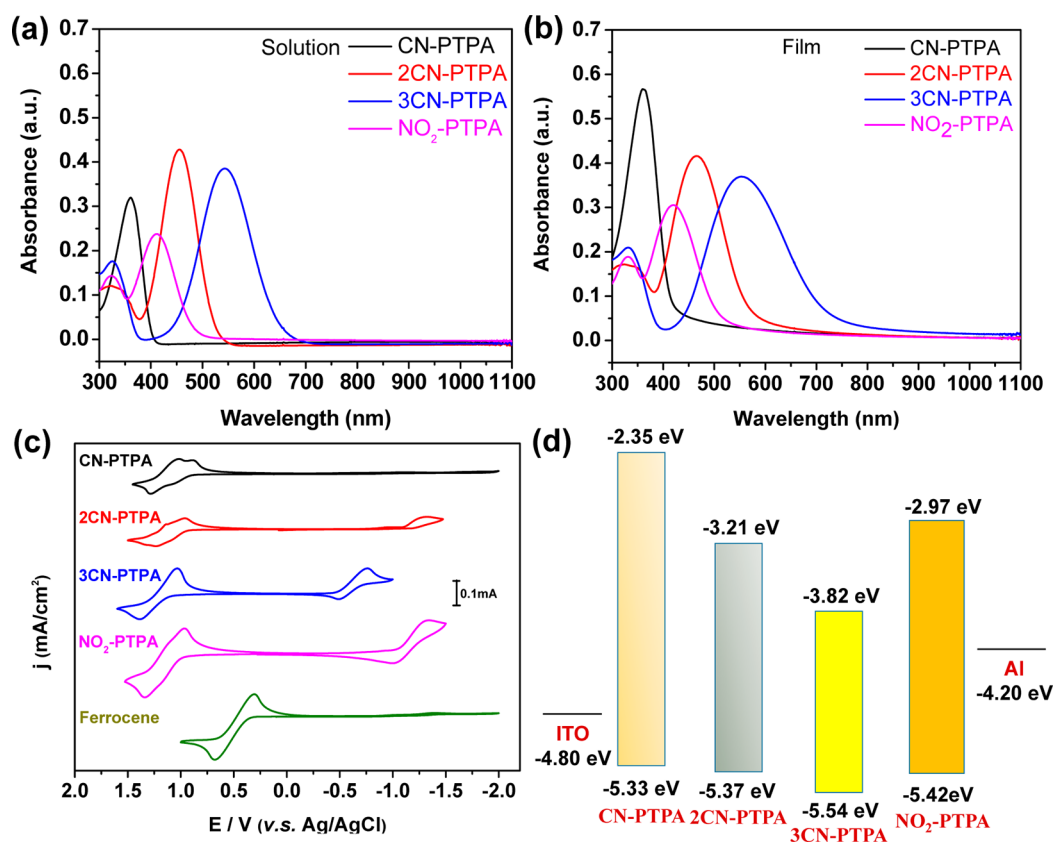


Figure 2. UV-vis spectra of the PTPAs (a) in CH_2Cl_2 solution ($10 \mu\text{M}$) and (b) in solid film ($40 \text{ nm} \pm 3$); (c) cyclic voltammetric diagrams of the PTPAs over cyclic scans in $0.1 \text{ M TBAPF}_6/\text{CH}_2\text{Cl}_2$ at a scan rate of 50 mV/s ; and (d) HOMO and LUMO energy levels of PTPAs.

Table 1. Redox Potentials and Energy Levels of the PTPAs

polymer	oxidation (V) ^a		reduction (V) ^a		λ_{onset}		$E_g^{\text{Opt}^b}$	$E_g^{\text{EC}^c}$	HOMO (eV) ^d	LUMO ^{Opt} (eV) ^e	LUMO ^{EC} (eV)
	E_{onset}	$E_{1/2}$	E_{onset}	$E_{1/2}$	solution	film					
CN-PTPA	0.91	1.10			404	416	2.98		5.33	2.35	
2CN-PTPA	0.95	1.11	-1.09	-1.24	535	573	2.16	2.04	5.37	3.21	3.33
3CN-PTPA	1.12	1.21	-0.49	-0.63	665	721	1.72	1.61	5.54	3.82	3.93
NO_2 -PTPA	1.00	1.15	-1.05	-1.17	482	505	2.45	2.05	5.42	2.97	3.37

^a vs Ag/AgCl in CH_2Cl_2 . ^b E_g^{Opt} (Optical band gap): Calculated from polymer films ($E_g = 1240/\lambda_{\text{onset}}$). ^c E_g^{EC} (Electrochemical band gap): Difference between HOMO^{EC} and LUMO^{EC}. ^dThe HOMO and LUMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV ; $E_{\text{onset}} = 0.38 \text{ V}$; $E_{1/2} = 0.49 \text{ V}$ in CH_2Cl_2). ^eLUMO^{Opt} (LUMO energy levels calculated from optical method): Difference between HOMO^{EC} and E_g^{Opt} .

CHCl_3 is a good choice as the processing solvent to fabricate high performance functional thin film by spin-coating or inkjet-printing process for further application such as optoelectronic devices and digital memory devices.

The thermal behavior of obtained polymers was recorded by TGA and DSC, and the thermal properties are summarized in Table S3 (SI). Typical TGA curves of the polymers are depicted in Figure S6 (SI) exhibiting high thermal stability with insignificant weight loss up to $410 \text{ }^\circ\text{C}$ under both nitrogen and air atmosphere. The decomposition temperature at a 10% weight-loss of these polymers in nitrogen and air were recorded in the range of $425\text{--}635$ and $420\text{--}630 \text{ }^\circ\text{C}$, respectively. The amount of carbonized residue (char yield) of these polymers in a nitrogen atmosphere was more than 65% at $800 \text{ }^\circ\text{C}$, leading a high limiting oxygen index (LOI) in the range of $43\text{--}47$.²⁵ The high char yields of these polymers can be ascribed to their high aromatic content. Typical DSC curves of PTPAs are depicted in Figure S7 (SI), and the glass-transition temperatures (T_g)

measured by the DSC were observed in the range of $159\text{--}278 \text{ }^\circ\text{C}$.

2.2. Optical and Electrochemical Properties. UV-vis absorption spectra of these polymers in CH_2Cl_2 solution ($10 \mu\text{M}$) and solid film (40 nm) coated on quartz substrate are depicted in Figure 2a,b, and the onset wavelengths of optical absorption in solid films were utilized to estimate the optical energy band gap (E_g) summarized in Table 1. PTPAs showed the absorption band around $325\text{--}362 \text{ nm}$ attributed to a $\pi\text{--}\pi^*$ transition of TPA moieties. 2CN-PTPA, 3CN-PTPA, and NO_2 -PTPA exhibited other bands around $412\text{--}543 \text{ nm}$ assigned to CT transitions between TPA and the substituent acceptors. The red shift absorption peaks from solutions to solid films could be ascribed to the molecular aggregation and enhanced intermolecular CT.

The electrochemical property of these polymers was investigated by cyclic voltammetry (CV), and the typical CV diagrams of PTPAs are depicted in Figure 2c. All the polymers

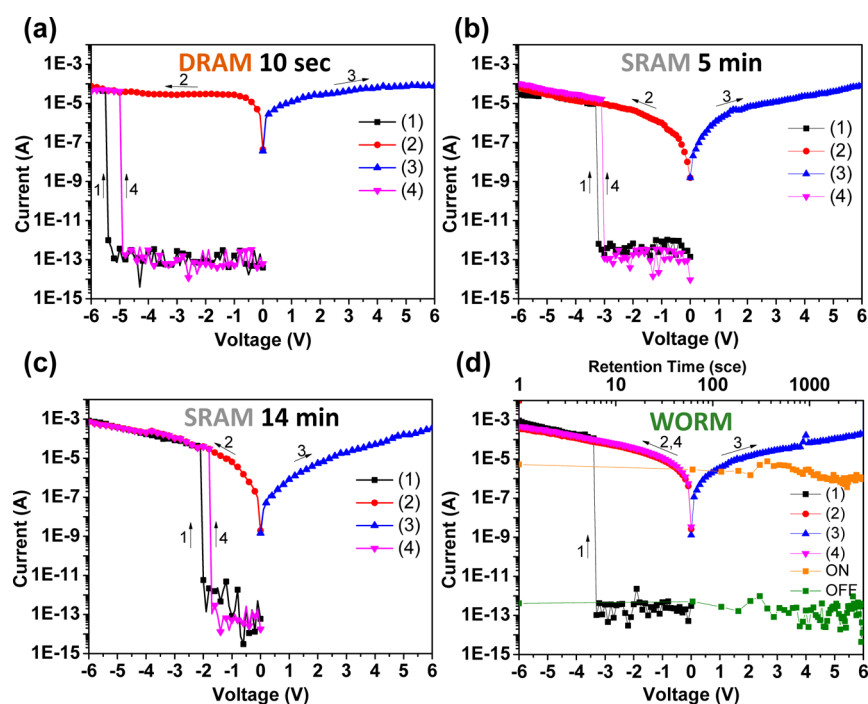


Figure 3. Current–voltage (I – V) characteristics of ITO/PTPAs/Al. (a) CN-PTPA, (b) 2CN-PTPA, (c) 3CN-PTPA, and (d) NO₂-PTPA with stability test.

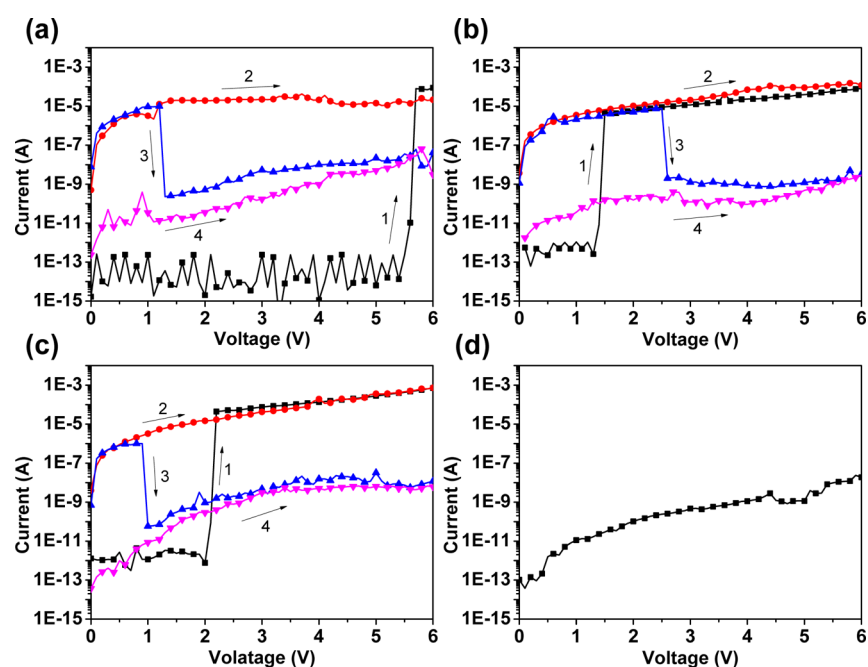


Figure 4. Positive sweep current–voltage (I – V) characteristics of (a) CN-PTPA, (b) 2CN-PTPA, (c) 3CN-PTPA, and (d) NO₂-PTPA.

exhibited one reversible oxidation redox couple, and oxidation potential of the PTPAs depended on the electron withdrawing ability of substituted cyano or nitro moieties. The anodic potential shift was observed as expectation when increased the number of cyano groups that enhance the acceptor strength and intramolecular CT between the donor and the acceptor moieties. In the reduction process, 2CN-PTPA and 3CN-PTPA showed reduction redox with onset potential (E_{onset}) around -1.09 and -0.49 V, respectively. The redox potentials of these polymers as well as their respective highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital

(LUMO) energy levels were calculated and summarized in Figure 2d and Table 1.

2.3. Memory Device Characteristics. The memory behaviors of PTPAs are depicted by current–voltage (I – V) characteristics of an ITO/polymer/Al sandwiched device as shown in Figure 3. The data stored by the polymeric memory devices was defined as the high- and low- conductivity response to external applied voltages. To avoid the thickness effect of the polymer film on memory properties, we adjusted the standard thickness (40 ± 3 nm). Figure 3a reveals I – V characteristics of CN-PTPA. The device was initially in the OFF state with the

current around 10^{-13} A, as the voltage sweeps from 0 to -5.2 V. When the applied bias increased to the switch-on voltage at -5.3 V, an abrupt increase in the current could be found, indicating the transition from the OFF state to ON state (writing process). The ON/OFF current ratio of the resulting memory device is up to 10^8 , which is high enough to avoid misreading in the application of digital data storage. The device also could remain in the ON state during the subsequent negative (the second sweep) and positive scans (the third sweep). The ON state would return to the OFF state just 10 s after removing the applied voltage, and could subsequently switch to ON state again at the threshold voltage of -5.0 V (the fourth sweep). Thus, the short retention time of the ON state indicates that CN-PTPA exhibits volatile dynamic random access memory (DRAM) memory behavior.

I - V curves of 2CN-PTPA are summarized in Figure 3b, and the device could be switched to the ON state with a sharp increasing of current ($\sim 10^7$) as the external applied voltage increased to its threshold voltage of -3.1 V during the first negative sweep. The reading process was conducted by the subsequent negative (the second sweep) and positive scans (the third sweep), implying the nonerasable characteristic of the device. The fourth sweep with a switch-on voltage of -3.0 V was observed after turning off the power for 5 min, indicating that the 2CN-PTPA-based memory device kept in the ON state for a longer time than CN-PTPA. The longer retention time at the ON state yet volatile as well as the randomly accessible ON and OFF states is analogy to volatile static random access memory (SRAM) memory behavior. The I - V characteristic of 3CN-PTPA shown in Figure 3c also reveals similar SRAM memory characteristic with longer retention time of 14 min.

I - V curves and retention time of the device derived from NO_2 -PTPA are summarized in Figure 3d and reveal similar curves with a threshold voltage of -3.3 V and an ON/OFF ratio of 10^7 . Once the NO_2 -PTPA memory device has been switched to the on state, it remained there even after turning off power over 1 h. In addition, stability of the device under a constant stress of -1 V is also shown in Figure 3d. There is no significant change at both ON and OFF states for 1 h under ambient air condition, indicating that the NO_2 -PTPA memory device is nonvolatile WORM memory device. Moreover, the memory device of NO_2 -PTPA-H (30 nm) also revealed the same WORM property as shown in Figure S8 (SI), implying that the memory behavior is independent of molecule weight of the applied material.

Furthermore, the positive unipolar switching behavior was also investigated and depicted in Figure 4. Except NO_2 -PTPA, all the devices derived from cyano-substituted polymers including CN-PTPA, 2CN-PTPA, and 3CN-PTPA could be switched to the ON state by positive scanning and exhibited WORM memory behavior (first and second sweep) as shown in Figure 4a–c. This phenomenon indicated that the Al atoms interact with the materials containing cyano preferentially over those containing nitro substituents, as reported in previous literature^{26,27} (Figure 4d). Therefore, the Al metal can possibly diffuse into the polymer layer under sufficiently thermal energy, and serve as the charge trap center. However, these devices returned to the off state after 5–10 cycles (third sweep) then could not be turned on again (fourth sweep), which is not clear at the present stage.

2.4. Proposed Switching Mechanism. To get more insight into the different memory behavior of these PTPA-based devices, we carried out molecular simulation on the basic

three repeat unit by DFT/B3LYP/6-31G(d) with Gaussian 09 program. The charge density isosurfaces and the most energetically favorable geometry of PTPAs are summarized in Figure 5. For all PTPAs, the HOMO energy levels were located

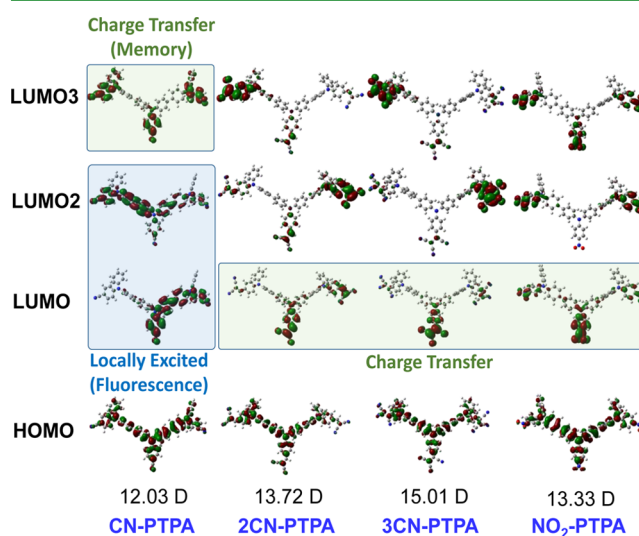


Figure 5. Calculated molecular orbitals and corresponding energy levels of three basic repeat units of the PTPAs.

mainly at the electron-donating TPA moieties, while the LUMO energy levels were located at different units, depending on the electron withdrawing ability. For CN-PTPA, the LUMO energy levels could be located at TPA main chain resulting in high PLQY (Figure 6), which could be attributed to the π - π^*

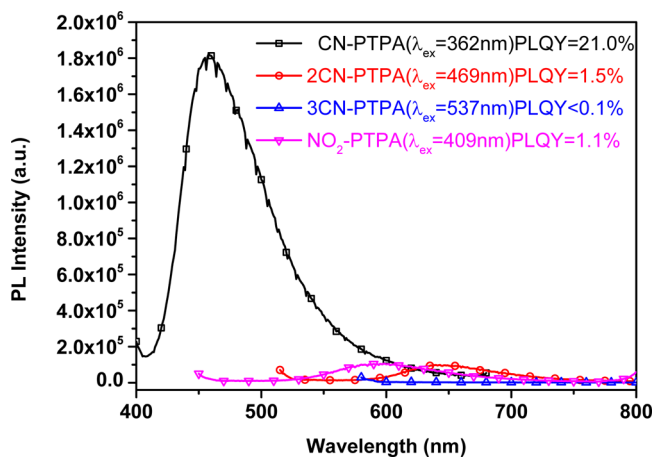


Figure 6. Photoluminescence spectra of PTPA thin films.

locally excited states and should result in no memory behavior. However, according to previous literatures, when the applied electric field reaches the switching-on voltage, some electrons at the HOMO accumulate energy and transit to the LUMO to form a charge transfer complex (ON state) by different ways.²⁸ Therefore, CT complex could also be obtained from HOMO of TPA main chain to the upper excited state LUMO3 under higher external applied voltage. Thus, CN-PTPA memory device reveals volatile DRAM due to large band gap and weak CT capability of the ambipolar polymer structure, while 2CN-PTPA and 3CN-PTPA exhibited longer retention time (SRAM) than CN-PTPA attributed to the higher CT capability

and dipole moment from the π - π conjugated cyanovinyl groups. For NO₂-PTPA, the LUMO surfaces were delocalized around nitro group with larger energy band gap and lower dipole moment than those of 2CN-PTPA and 3CN-PTPA. However, NO₂-PTPA exhibited WORM memory behavior even nitro substituent with weaker electron withdrawing ability than cyanovinyl groups. This phenomenon could be ascribed to the strong trap capability of nitro group and lower conjugation between nitro and phenyl group, the charge could be transferred from donor of TPA moiety to nitro acceptor group under applied bias, resulting in charge trapping within nitro substituent and hard to relax back to the donor surface.

3. CONCLUSIONS

A series of poly(triphenylamine)s with different acceptor substituents have been readily synthesized and revealed interesting memory behavior. The devices with the sandwiched structure of ITO/PTPAs/Al exhibited tunable volatile and nonvolatile switching characteristics due to the charge transfer effect between the TPA donor moiety and pendant acceptor substituents. The volatile memory behavior with different retention time could be manipulated from DRAM (CN-PTPA) to SRAM (2CN-PTPA and 3CN-PTPA) with different retention times. In addition, NO₂-PTPA revealed nonvolatile WORM behavior due to a charge that could be trapped tightly within nonconjugated nitro acceptor unit. This comparative study of the substituents and charge transfer effect may provide some guiding for designing new high-performance D-A polymeric data storage devices in the future.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental section; table of molecular weights, solubility behavior, thermal properties; NMR, FTIR, TGA, DSC, and current-voltage (I - V) characteristics. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b04123.

■ AUTHOR INFORMATION

■ Corresponding Author

* Tel: 886-2-33665070. Fax: 886-2-33665237. E-mail: gsliau@ntu.edu.tw.

■ Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are grateful acknowledge to the Ministry of Science and Technology of Taiwan for the financial support.

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