

Polyfluorene-Based Push–Pull Type Functional Materials for Write-Once-Read-Many-Times Memory Devices

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A highly soluble polyfluorene-based copolymer containing electron-rich triphenylamine (TPA) and electron-poor 9,9-bis(3,4-bis(3,4-dicyanophenoxy)phenyl side chains in the C-9 position of the fluorene unit was synthesized under Yamamoto conditions. By applying 306 nm as excitation wavelength, the resultant polymer exhibits strong photoluminescence with maximum emission peaks centered at 413 and 433(sh) nm in chloroform. The calculated highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), energy bandgap, ionization potential, and electron affinity are -5.66, -3.44, 2.22, 5.92, and 3.70 eV, respectively. The as-fabricated polymer film exhibited typical stable write-once-read-manytimes (WORM) memory characteristics, which are desirable for ultralow-cost permanent storage of digital images. The currents in both ON and OFF states did not show any degradation, suggesting good device stability. The ON/OFF current ratio observed in the sweep I-V characteristics at +1.0 V is 6.1×10^3 . The conduction mechanism through ITO/polymer/Al device is discussed.

Introduction

One of the aims of the investigations into the donoracceptor (D-A) type polymers, in which the hybridization of the energy levels of the donor and acceptor moieties result in D-A systems with unusually low highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) separation,¹ is to construct artificial systems that mimic the electron transfer lying at the heart of photosynthetic solar energy conversion and in developing molecular electronics.^{1–12} Some known electron withdrawing groups, for example, cyano, nitro, quinoxalines, pyrazines, thiadiazoles, TCNO, AIDCN, F_{16} PcCu, C_{60} and others, have been widely used in the

- (2) Saricifici, N. S.; Smilowitz, L.; Heeger, A. J.; Wadul, F. Science 1992, 258, 1474–1476.
- (3) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. Science 1995, 270, 1789-1791.
- (4) Granstrom, M.; Petritsch, K.; Arias, A. C.; Lux, A.; Andersson, M. R.; Friend, R. H. *Nature* 1998, 395, 257–260.
 (5) Giacalone, F.; Martin, N. *Chem. Rev.* 2006, 106, 5136–5190.
 (6) Luzzati, S.; Scharber, M.; Catellani, M.; Giacalone, F.; Segura, S. Scharber, M.; Catellani, M.; Giacalone, F.; Segura, Scharber, M.; Catellani, M.; Giacalone, Scharber, M.; Catellani, M.; Giacalone, Scharber, M.; Catellani, M.; Giacalone, Scharber, M.; Catellani, M.; Catell
- J. L.; Martin, N.; Neugebauer, H.; Sacriciftci, N. S. J. Phys. Chem. B 2006, 110, 5351-5358
- (7) Gomez, R.; Blanco, R.; Veldman, D.; Segura, J. L.; Janssen, R. A. J. J. Phys. Chem. B 2008, 112, 4953-4960.
- (8) El-Khouly, M. E.; Chen, Y.; Zhuang, X. D.; Fukuzumi, S. J. Am. *Chem. Soc.* **2009**, *131*, 6370–6371. (9) Lin, Y.; El-Khouly, M. E.; Chen, Y.; Supur, M.; Gu, L.; Li, Y.;
- Fukuzumi, S. *Chem.—Eur. J.* 2009, *15*, 10818–10824.
 (10) Chen, Y.; El-Khouly, M. E.; Zhuang, X. D.; He, N.; Araki, Y.; Lin, Y.; Ito, O. *Chem.—Eur. J.* 2007, *13*, 1709–1714.
- (11) Chen, Y.; EI-Khouly, M. E.; Araki, Y.; Ito, O. Org. Lett. 2005, 7, 1613-1616.
- (12) Zhao, H.; Yuan, W. Z.; Mei, J.; Tang, L.; Liu, X. Q.; Yan, J. M.; Shen, X. Y.; Sun, J. Z.; Qin, A.; Tang, B. Z. J. Polym. Sci. A: Polym. Chem. 2009, 47, 4995-5005.

optoelectronic and photonic devices. In our previous work, we designed a series of pull-push type functional polymers, including C₆₀-PDPAF-C₆₀,¹⁰ CNF-TPA,⁹ DR1-PDPAF-DR1,^{8,13} TPAPAM-GO (GO: graphene oxide),¹⁴ and GO-PVK.¹⁵ Memory devices based on the last three materials exhibit typical bistable electrical switching and nonvolatile rewritable memory effect, with an ON/OFF state current ratio of more than 10^3 . Both the ON and OFF states are stable under a constant voltage stress and survived up to 10^8 read cycles at a small read voltage.

As a type of nonvolatile memory that is capable of holding data permanently and being read from repeatedly, the write-once-read-many-times (WORM) memory is very desirable for ultralow-cost permanent storage of digital images, eliminating the need for slow, bulky, and expensive mechanical drives used in conventional magnetic and optical memories.¹⁶⁻²⁰ Basically the WORM

- (13) Ling, Q. D.; Kang, E. T.; Neoh, K. G.; Chen, Y.; Zhuang, X. D.; Zhu, C.; Chan, D. S. H. Appl. Phys. Lett. 2008, 92, 143302/1– 143302/3
- (14) Zhuang, X. D.; Chen, Y.; Liu, G.; Li, P. P.; Zhu, C. X.; Kang, E. T.; Noeh, K. G.; Zhang, B.; Zhu, J. H.; Li, Y. X. Adv. Mater. 2010, 22, 1731 - 1732
- (15) Liu, G.; Zhuang, X. D.; Chen, Y.; Zhang, B.; Zhu, J. H.; Zhu, C. X.; Neoh, K. G.; Kang, E. T. Appl. Phys. Lett. 2009, 95, 253301/ 1-253301/3.
- (16) Choi, S.; Hong, S. H.; Cho, S. H.; Park, S.; Park, S. M.; Kim, O.; Ree, M. *Adv. Mater.* **2008**, *20*, 1766–1771. (17) (a) Möller, S.; Perlov, C.; Jackson, W.; Taussig, C.; Forrest, S. R.
- Nature 2003, 426, 166–169. (b) Ling, Q. D.; Liaw, D. J.; Zhu, C. X.; Chan, D. S. H.; Kang, E. T.; Neoh, K. G. Prog. Polym. Sci. 2008, 33, 917-978.
- (18) Mukherjee, B.; Pal, A. J. *Chem. Mater.* 2007, *19*, 1382–1387.
 (19) Liu, G.; Ling, Q. D.; Teo, E. Y. H.; Zhu, C. X.; Chan, D. S. H.;
- Neoh, K. G.; Kang, E. T. *ACS Nano* **2009**, *3*, 1929–1937. Kim, D. M.; Park, S.; Lee, T. J.; Hahm, S. G.; Kim, K.; Kim, J. C.; (20)Kwon, W.; Ree, M. Langmuir 2009, 25, 11713-11719.

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memory functions as conventional CD-R, DVD-R, or programmable read-only memories(PROMs). Choi et al.¹⁶ reported a new cyano-rich hyperbranched copper phthalocyanine polymer (HCuPc) which is thermally stable up to 450 °C. The device based on the HCuPc polymer exhibited excellent WORM memory characteristics and reliability, even in air ambient conditions. However, it should be worth noting that, from the molecular structure of HCuPc the authors have given, this material might have the relatively low solubility in common organic solvents because of the strong $\pi - \pi$ stacking effect between the coplanar phthalocyanine rings, giving rise to a technical difficulty in the fabrication of large-area thin film devices by spin- or blade-coating a solution in organic solvent. On the other hand, it would also be difficult to control and/or adjust the content of the electron-withdrawing cyano groups in the polymer structure, which may have an important influence on the memory performance of the devices, especially in such a device based on the D-A type polymers. Recently we reported a novel WORM device by spin-coating a preassembled solution of D-A type Dispersed Red-1(DR1)grafted poly(N-vinylcarbazole) (PVDR) as the active layer sandwiched between Al and ITO electrodes.²¹ Upon selfassembly, the nanoaggregated PVDR film displays helical columnar stacks with large grain sizes, whereas a nonnanoaggregated PVDR film exhibits an amorphous morphology with smaller grain size. This device shows very good memory performance, with an ON/OFF current ratio of more than 10^5 and a low misreading rate through the precise control of the ON and OFF states. The stability of the nanoaggregated PVDR device is much higher than that of the non-nanoaggregated PVDR device. This difference in device stability under constant voltage stress can be mainly attributed to the difference in the film crystallinity and surface morphology. In this study, we designed and synthesized a highly soluble polyfluorene-based polymer 6 containing electron-rich triphenylamine and electron-poor 9,9-bis(3,4bis(3,4-dicyanophenoxy)phenyl side chains in the C-9 position of fluorene unit, as shown in Scheme 1. This material exhibits typical WORM memory characteristics, with long retention time of more than 3000 s without any degradation and high ON/OFF ratio of 6×10^3 . In contrast to the hyperbranched HCuPc polymer,¹⁶ the content of the cyano groups in the polymer structure can be easily controlled by adjusting the monomer levels used for polymerization.

Experimental Section

General Procedures. The operations for synthesis prior to the termination reaction were carried out under purified argon. All chemicals were purchased from Aldrich and used without further purification. Organic solvents were purified, dried, and distilled under dry nitrogen.

The UV/vis absorption spectral measurements were carried out with a Shimadzu UV-2450 spectrophotometer. FTIR spectra were recorded on a Nicolet Nagma-IR 550 spectrophotometer using KBr pellets. Thermal properties of the samples

Scheme 1. Synthesis of 3, 5, and 6



were measured using a Perkin-Elmer Pyris 1 thermogravimetric analyzer in flowing (100 mL.min⁻¹) nitrogen atmosphere. Steady-state fluorescence spectra were measured on a Shimadzu RF-5300 PC spectrofluoro-photometer equipped with a photomultiplier tube having high sensitivity in the 700-800 nm region. The sample for the fluorescence measurement was dissolved in the dry chloroform, filtered, transferred to a long quartz cell, and then capped and bubbled with high pure argon(without O₂ and moisture) for 10 min before measurement. Gel permeation chromatography trace of the samples were recorded on a Viscotek T60A/LR40 GPC system. Tetrahydrofuran (THF) was used as the eluent, and linear polystyrene was used as the standard.

Cyclic voltammetry was performed on an ALS630B electrochemical analyzer in deaerated benzonitrile containing recrystallized tetrabutylammonium perchlorate (Bu_4NCIO_4 , 0.1 M) as the supporting electrolyte at 298 K. A conventional threeelectrode cell was used with a platinum working electrode (surface area of 0.3 mm²) and a platinum wire as the counter electrode. The Pt working electrode (Bioanalytical System-(BAS), Inc.) was routinely polished with BAS polishing alumina suspension and rinsed with acetone before use. The measured potentials were recorded with respect to the Ag/AgNO₃ (0.01 M) reference electrode. All electrochemical measurements were carried out under an atmospheric pressure of argon.

Device Fabrication. The Indium tin oxide (ITO) glass substrate was carefully precleaned sequentially with deionized water, acetone, and 2-propanol in an untrasonic bath for 15 min, and then treated with oxygen plasma. A dimethylformamide (DMF, 6 mL)/toluene (2 mL) solution of polymer **6** (6.4 mg) was spin-coated (1000 rpm, 40 s) onto the ITO substrate, followed by the removal of the solvent in a vacuum

⁽²¹⁾ Zhuang, X.D.; Chen,Y.; Liu,G.; Zhang,B.; Neoh, K. G.; Kang, E. T.; Zhu, C. X.; Li,Y. X.; Niu, L. J. Adv. Funct. Mater. 2010, in press, DOI: 10.1002/adfm.201000258.

chamber at 10^{-5} Torr at 100 °C for 5 h. The thickness of the polymer layer was about 50 nm. Finally, a 300 nm-thick Al top electrode was thermally evaporated at a pressure around 10^{-7} Torr through a shadow mask. The measurements were carried out on devices of four $3 \times 3 \text{ mm}^2$ in size. The current–voltage (I-V) characteristics were performed using a Keithley 2400 sourcemeter controlled by a computer, and the positive voltage was applied to the top Al electrode. All the electrical measurements were carried out in ambient condition without any device encapsulation.

Synthesis of 4,4'-(2,7-Dibromo-9*H*-fluorene-9,9-diyl)dibenzene-1,2-diol (3). A stirred mixture of 2,7-dibromofluorenone (3.1 g, 9 mmol), pyrocatechol (5.0 g, 45 mmol), and methanesulfonic acid (2.7 mL, 40 mmol) in CCl₄ (20 mL) was heated at 80 °C for 40 h. After cooling to room temperature, the reaction mixture was filtered, washed with a large amount of CH₂Cl₂, and then reprecipitated from acetone to produce 2.56 g of gray powder (yield 52.7%). ¹H NMR (DMSO-*d*₆, 500 MHz): δ /ppm = 6.32 (dd, 2H), 6.49 (d, 2H), 6.60 (d, 2H), 7.42 (s, 2H), 7.57 (dd, 2H), 7.88(d,2H), 8.85(s,2H), 8.89(s,2H); Elemental Analysis (EA): calcd for C₂₅H₁₆-Br₂O₄(537.94 g/mol) C55.58; H2.99, found C55.65; H3.38; MS (EI): *m*/*z* 538.00 (M⁺).

Synthesis of 9,9-Bis[3,4-bis(3,4-dicyanophenoxy)phenyl]-2,7dibromo-9H-fluor-ene (4). A mixture of 3 (1.61 g, 3.0 mmol), 4-nitrophthalonitrile (2.08 g, 12.0 mmol), and K₂CO₃ (1.66 g, 12.0 mmol) in anhydrous dimethyl sulfoxide (DMSO, 30 mL) was stirred at 25 °C for 20 h. With completion of the reaction, the mixture was poured into 200 mL of cold dilute HCl. The collected crude product was washed with water until neutral, and then redissolved in CH2Cl2 (100 mL), washed with 5% NaOH solution (400 mL) and water (100 mL), respectively. The organic layers were dried over MgSO₄ and filtered. Evaporation of the solvent was followed by column chromatography (SiO₂, ethyl acetate/petroleum ether(v/v 1:4) as eluant, Rf = 0.22). A pale yellow solid obtained was thoroughly vacuumdried at 40 °C overnight. Yield 1.28 g (41%). ¹H NMR (DMSO d_6): δ /ppm = 6.91(dd, 2H), 7.29 (d, 2H), 7.32 (dd, 2H), 7.35 (dd, 2H), 7.66 (d, 2H), 7.68-7.73(m,6H), 7.73(d, 2H), 7.89 (d, 2H), 8.00 (d, 4H); 13 C NMR (DMSO- d_6): δ 64.5, 108.9, 109.3, 115.4, 115.7,116.0, 116.2, 116.8, 117.0, 121.3, 121.8, 122.1, 123.6, 123.7, 124.6, 126.7, 129.2, 132.1, 136.3, 136.5, 138.3, 144.2, 144.4, 144.7, 152.1, 160.3, 161.0; EA calcd for C₅₇H₂₄N₈O₄Br₂: C65.53, N10.73, H2.32; found C63.98, N10.28, H2.02.

Synthesis of 9,9-Bis(4-diphenylaminophenyl)-2,7-dibromofluorene (5). To a stirred mixture of 2,7-dibromofluorenone (1.72 g, 5.10 mmol) and triphenylamine (17.5 g, 0.071 mol) was added methane sulfonic acid (0.49 g, 5.10 mmol) under a purifed argon atmosphere, and then reacted at 140 °C for 6 h. After cooling to the room temperature, the dichloromethane extract was washed with Na₂CO₃ solution until the aqueous layer reached neutral, and then dried over anhydrous MgSO₄ and filtered. Evaporation of the solvent was followed by column chromatography (SiO₂/ hexane-CH₂Cl₂). The obtained product was recrystallized from acetone to give the TPA-substituted 2,7dibromofluorene (2.95 g,70%). FDMS: m/z = 811[M+]; UV/ vis(in CHCl₃): $\lambda/nm = 256$, 310, 322; ¹H NMR (in CDCl₃): $\delta/ppm = 6.99(m, 20H, aryl H)$, 7.22(m,8H, aryl H), 7.46(dd,2H), 7.51(d,2H),7.56(d,2H).

Synthesis of the Copolymer 6. A mixture of $Ni(COD)_2$ (620 mg, 2.2 mmol), 2,2-bipyridine (348 mg, 2.2 mmol), and 1,5-cyclooctadienyl(0.3 mL,2.2 mmol) in dry DMF (12 mL) was stirred at 75 °C for 30 min under an argon atmosphere. To the above solution was added a solution of **5** (1.57 g, 1.93 mmol) and **4** (72 mg, 0.07 mmol) in dry toluene (15 mL)/DMF(5 mL).

After heating at 80 °C for 24 h, an excess of bromobenzene (2 g,12.74 mmol) was added in the above reaction system, followed by additional reaction at the same temperature for 24 h. The reaction mixture was poured into a methanol/HCl(2:1) solution. The collected crude product was dissolved in CHCl₃, reprecipitated from methanol/acetone(4:1), and then subject to a Soxhlet extraction with acetone to give the target product **6** (300 mg, 47%). GPC: $M_n = 1.1 \times 10^4$, $M_w/M_n = 4.4$; UV/vis (in CHCl₃): $\lambda_{max} = 236$, 306 nm; PL (in toluene, $\lambda_{ex} = 306$ nm): $\lambda_{max} = 411$ nm.

Results and Discussion

Fluorene-based polymers and oligomers have emerged as one of the most promising materials owing to their high photoluminescence quantum yields, good charge transport properties, and better thermal and chemical stability.²² The classical poly(alkylfluorene) homopolymers suffer from poor spectral stability associated with keto-defects in the polymer backbone or excimer emission.²³ The common strategies, to address this issue, are the introduction of bulky groups to the C-9 position of the fluorene unit, for example, spirobifluorene, or copolymerization with suitable comonomers.²⁴ A large number of theoretical and experimental results have demonstrated that the facile functionalization at the C-9 position of the fluorene unit may offer an opportunity to reduce the interchain interactions thereby improving the electric, optoelectronic, and photonic properties of the resulting polymers. In our previous work,²⁵ we prepared a novel conjugated PFO/PPV copolymer containing the pendant bis(4-alkoxyphenyl) groups in the C-9 position of every fluorene unit through a typical Heckcouping reaction. The resulting polymer exhibits very strong photoluminescence with maximum emission peaks centered at 474 nm in dilute benzonitrile, and a single glass-transition temperature at about 95 °C. The excited triplet-state

- (23) (a) Grell, M.; Bradley, D. D. C.; Ungar, G.; Hill, J.; Whitehead, K. S. *Macromolecules* 1999, 32, 5810–5817. (b) Jenekhe, S. A.; Osaheni, J. A. *Science* 1994, 265, 765–768.
- (24) (a) Ego, C.; Grimsdale, A. C.; Uckert, F.; Yu, G.; Srdanov, G.; Müllen, K. Adv. Mater. 2002, 14, 809–811. (b) Yoon, K.-J.; Park, J. S.; Lee, S.-J.; Song, M.; Shin, I. A.; Lee, J. W.; Gal, Y.-S.; Jin, S.-H. J. Polym. Sci. A: Polym. Chem. 2008, 46, 6762–6769. (c) Klärmer, G.; Lee, J. I.; Lee, V. Y.; Chan, E.; Chen, J. P.; Nelson, A.; Markiewicz, D.; Siemens, R.; Scott, J. C.; Miller, R. D. Chem. Matter. 1999, 11, 1800–1805. (d) Bondarev, D.; Zedni'k, J.; Vohli'dal, J.; Podha'jecka', K.; Sedla'ček, J. J. Polym. Sci. A: Polym. Chem. 2009, 47, 4532–4546. (e) Horst, S.; Evans, N. R.; Bronstein, H. A.; Williams, C. K. J. Polym. Sci. A: Polym. Chem. 2009, 47, 5116–5125. (f) Chen, R.-T.; Chen, S.-H.; Hsieh, B.-Y.; Chen, Y. J. Polym. Sci. A: Polym. Chem. 2009, 47, 2821–2834.
- Chen, Y. J. Polym. Sci. A: Polym. Chem. 2009, 47, 2821–2834.
 Chen, Y.; Araki, Y.; Doyle, J.; Strevens, A.; Ito, O.; Blau, W. J. Chem. Mater. 2005, 17, 1661–1666.

 ^{(22) (}a) Scherf, U.; List, E. J. W. Adv. Mater. 2002, 14, 477–487. (b) Geng, Y.; Culligan, S. W.; Trajkovska, A.; Wallace, J. U.; Chen, S. H. Chem. Mater. 2003, 15, 542-549. (c) Li, J. Y.; Ziegler, A.; Wegner, G. Chem.-Eur. J. 2005, 11, 4450-4457. (d) Muller, C. D.; Falcou, A.; Reckefuss, N.; Rojahn, M.; Wiederhirn, V.; Rudati, P.; Frohne, H.; Nuyken, O.; Becker, H.; Meerholz, K. Nature 2003, 421, 829-833. (e) Wang, X. J.; Perzon, E.; Oswald, F.; Langa, F.; Admassie, S.; Andersson, M. R.; Inganas, O. Adv. Funct. Mater. 2005, 15, 1665-1670. (f) Ashraf, R. S.; Hoppe, H.; Shahid, M.; Gobsch, G.; Sensfuss, S.; Klemm, E. J . Polym. Sci. A: Polym. Chem. 2006, 44, 6952-6961. (g) Mcneill, C. R.; Halls, J. J. M.; Wilson, R.; Whiting, G. L.; Berkebile, S.; Ramsey, M. G.; Friend, R. H.; Greenham, N. C. Adv. Funct. Mater. 2008, 18, 2309-2321. (h) Tang, W.; Chellappan, V.; Liu, M.; Chen, Z.-K.; Ke, L. ACS Appl. Mater. Interfaces 2009, 1, 1467-1473. (i) Lim, E.; Kim, Y. M.; Lee, J.-I.; Jung, B.-J.; Cho, N. S.; Lee, J.; Do, L.-M.; Shim, H.-K. J. Polym. Sci. A: Polym. Chem. 2006, 44, 4709-4721

maximum of the polymer occurs in the region of 460-540 nm with a lifetime of 65.8 μ s. In this study, as shown in Scheme 1, the acid-catalyzed condensation reaction of 2,7dibromo-9-fluorenone (1) with excess pyrocatechol gives 4,4'-(2,7-dibromo-9H-fluorene-9,9-diyl)dibenzene-1,2-diol (3, 52.7%), which was used to react with 4-nitrophthalonitrile to produce compound 4(41%) in the presence of anhydrous K₂CO₃. Condensation of 2,7-dibromofluorenone with a large excess of triphenylamine (TPA) in methanesulfonic acid gives 9,9-bis(4- diphenylamino- phenyl)-2,7-dibromofluorene(5) in a yield of 70%. As one of the useful hole transporting materials, TPA and its organic and/or polymeric derivatives have been widely used in optoelectronic devices because of their low ionization potentials, tridimensional steric, and good UV-light harvesting properties.²⁶ The polymerization of monomers 4 and 5 was carried out under Yamamoto-coupling conditions to give a soluble D-A type polymer 6 in good yield. It should be noted that the synthesis employs an excess of bromobenzene to remove any residual bromine functionalities. The resultant polymer has a number average molecular weight (M_n) of 1.1×10^4 , with a polydispersity of 4.4.

To dermine the ratio of x to y in the polymer structure by the ¹H NMR spectroscopy, the cyano groups in the polymer needs to be converted to the carboxyl groups first by hydrolysis of 6 accomplished with hydrochloric acid alone.²⁷ In a typical procedure, **6** was added into a concentrated HCl solution. After stirring at room temperature for 10 h, the reaction mixture was poured into a MeOH/H₂O (v/v 90:10) solution. The collected crude product was washed with a large amount of water until the aqueous layer reached neutral, followed by the vacuum-dry at 40 °C overnight. The obtained resulting polymer with carboxyl groups has good solubility in chloroform, but a little bit dissolves in DMSO. In the ¹H NMR spectrum of 6the proton signal of CDCl₃ at $\delta = 7.24$ ppm in general overlaps with the signals for the aromatic protons. To avoid the influence of its proton signal on the integral measurements, the ¹H NMR spectrum of **6** was done in a mixture of CDCl₃ and DMSO- d_6 (v/v 1:2). In this case, the signal of CDCl₃ appears at $\delta = 8.10$ ppm (in the literature²⁸ the proton signal of chloroform is located at $\delta = 8.32$ ppm in the presence of deuterated DMSO), as shown in Figure 1. The integral ratio of the signals of the total carboxyl protons to the total aromatic protons is about 2:71, from which the ratio of x to y can be roughly estimated as 9:91.



Figure 1. ¹H NMR spectrum of the sample in DMSO- d_6 /CDCl₃ (v/v 2:1).



Figure 2. UV/vis absorption and photoluminescence ($\lambda_{ex} = 306$ nm) spectra of the polymer 6 in dilute CHCl₃.

As shown in Figure 2, the main absorption peak in the UV/vis spectrum of 6 is located at 306 nm because of the $n-\pi^*$ transition of the triphenylamine moiety.²⁹ By applying 306 nm as excitation wavelength, the polymer 6exhibits strong photoluminescence with maximum emission peaks centered at 413 and 433(sh) nm in chloroform. The observed larger Stokes shift for the sample (8408 cm^{-1}) is associated with a substantial change of the geometric structure from the ground state (S_0) to the first excited state $(S_1)^{30}$ as a result of an intramolecular charge transfer (ICT) or excited-state proton transfer.³¹

The electrochemical measurement was carried out using cyclic voltammetry (CV) in deaerated acetonitrile containing recrystallized Bu₄NClO₄(0.1M) at room temperature (Figure 3). The potentials were measured against Ag/AgCl as reference electrode. All potentials (vs Ag/ Ag⁺) were converted to values versus SCE by adding 0.29 V.³² The first oxidation and reduction potentials for 6 were found to be as +1.24 versus Ag/Ag⁺ that corresponds to +1.53 V versus SCE, and -0.98 V versus Ag/Ag⁺ that corresponds to -0.69 V versus SCE, respectively. The HOMO and LUMO values of 6 were experimentally calculated by the onset of the redox potentials taking the known reference level for ferrocene, 4.8 eV below the

^{(26) (}a) Lin, H. Y.; Liou, G. S.; Lee, W. Y.; Chen, W. C. J. Polym. Sci. A: Polym. Chem. 2007, 45, 1727-1736. (b) Fang, Q.; Tamamoto, T. Macromolecules 2004, 37, 5894-5899. (c) Chen, C. H.; Shi, J.; Tang, C. W. Macromol. Symp. 1997, 125, 1-48. (d) Park, J. H.; Cho, N. S.; Young, K. J.; Cho, H. J.; Shim, H. K.; Kim, H.; Lee, Y. S. Org. Electron. 2007, 8, 272-285.

 ⁽²⁷⁾ Miller, C. A.; Long, L. M. J. Am. Chem. Soc. 1951, 73, 4895–4898.
 (28) (a) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. J. Org. Chem. 1997, 62, 7512–7515. (b) Jacobson, N. E. NMR Spectroscopy Explained: Simplified Theory, Applications and Examples for Organic Chem-

<sup>istry and Structural Biology; Wiley: Hoboken, NJ, 2007.
(29) (a) Chen, Y.; Lin, Y.; Ei-Khouly, M. E.; He, N.; Yan, A. X.; Liu, Y.; Cai, L. Z.; Ito, O. J. Polym. Sci. A: Polym. Chem. 2008, 46,</sup> 4249-4253. (b) Bolognesi, A.; Betti, P.; Botta, C.; Destri, S.; Giovanella, U.; Moreau, J.; Pasini, M.; Porzio, W. *Macromolecules* **2009**, *42*, 1107–1113. (c) Lu, J. J.; Shen, P.; Zhao, B.; Yao, B.; Xie, Z. Y.; Liu, E. H.; Tan, S. T. Eur. Polym. J. 2008, 44, 2348-2355.

⁽³⁰⁾ Wang, B. C.; Liao, H. R.; Yeh, H. C.; Wu, W. C.; Chen, C. T. J.

 ⁽³⁰⁾ Wang, B. C., Elao, H. K., Feli, H. C., Wu, W. C., Chen, C. T. J. Lumin. 2005, 113, 321–328.
 (31) Peng, X.; Song, F.; Lu, E.; Wang, Y.; Zhou, W.; Fan, J.; Gao, Y. J. Am. Chem. Soc. 2005, 127, 4170–4171.
 (32) Mann, C. K.; Barnes, K. K. Electrochemical Reactions in Nonaqu-

eous Systems; Marcel Dekker: New York, 1990.



Figure 3. Cyclic voltammogram of the polymer film coated on platinum plate electrode in deaerated CH_2Cl_2 containing Bu_4NClO_4 (0.1 M). Sweep rate: 100 mV s⁻¹.

vacuum level, according to the eq 1:11,33

HOMO/LUMO =
$$-[E_{\text{onset}} - E_{\text{ox.(ferrocene)}}] - 4.8 \text{ eV}$$
 (1)

In our electrochemical experiments ferrocene exhibits an oxidation peak with an onset of 0.38 V versus Ag/AgCl. The calculated HOMO, LUMO, and bandgap values were -5.66, -3.44, and 2.22 eV, respectively. The values of the ionization potential (IP) and the electron affinity (EA) can also be estimated from these onset potentials (vs SCE) using eqs 2,3:³⁴

$$IP = E_{\text{first oxidation}} + 4.39 \text{ eV}$$
(2)

$$EA = E_{\text{first reduction}} + 4.39 \text{ eV}$$
 (3)

Where the constant 4.39 eV is the relationship between IP, EA, and the electrochemical potentials.³⁵ The calculated IP and EA values are 5.92 and 3.70 eV, respectively.

For the memory device, the I-V characteristics (Figure 4) were measured by scanning the voltage from 0 to ± 5 V and back to 0 V, with grounded ITO. Starting with the high conductivity state where one can refer to it as the ON state in the as-fabricated device, the current increases slowly with the increase of the applied positive voltage, and then decreases abruptly at a critical bias (about 2.2 V). The device remains in the low current state, for example, OFF state, as the voltage is swept to higher value or back to -5 V. In other words, the low OFF state is retained permanently in the subsequent voltage sweeps. This irreversible nature of the transition from a high conduction to a low conduction

- (33) (a) Wu, T. Y.; Sheu, R. B.; Chen, Y. *Macromolecules* 2004, *37*, 725–733. (b) Kunter, W.; Noworyta, K.; Deviprasad, G. R.; Souza, F. D. J. Electrochem. Soc. 2000, 147, 2647–2651.
- (34) (a) Pei, J.; Ni, J.; Zhou, X.; Cao, X.; Lai, Y. J. Org. Chem. 2002, 67, 8104–8113. (b) Kumaresan, D.; Thummel, R. P.; Bura, T.; Ulrich, G.; Ziessel, R. Chem.—Eur. J. 2009, 15, 6335–6339. (c) Chen, Z. K.; Huang, W.; Wang, L. H.; Kang, E. T.; Chen, B. J.; Lee, C. S.; Lee, S. T. Macromolecules 2000, 33, 9015–9025. (d) Yang, C.; Jenekhe, A. S. Macromolecules 1995, 28, 1180–1196. (e) Iosip, M. D.; Destri, S.; Pasini, M.; Porzioc, W.; Pernstich, K. P.; Batlogg, B. Synth. Met. 2004, 146, 251–253.
- (35) (a) Frommer, J. E., Chance, R. R. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; John Wiley& Sons, Inc.: New York, 1986; Vol. 5, pp 462–507; (b) Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. J. Org. Chem. **1972**, 37, 916–918.



Figure 4. Typical I-V characteristics of the ITO/polymer 6/Al device.



Figure 5. Currents of ON and OFF states as a function of time for ITO/ polymer 6 (50 nm)/Al under a constant bias of +1 V. The ON/OFF current ratio as a function of the positive sweeping voltages is shown in the inset.

makes it suitable for WORM memory applications. Some functional materials^{16,36–38} also exhibited similar WORM

(38) (a) Lin, J.; Ma, D. J. Appl. Phys. 2008, 103, 024507/1–024507/4. (b) Yang, Y.; Ouyang, J.; Ma, L. P.; Tseng, R. J. H.; Chu, C. W. Adv. Funct. Mater. 2006, 16, 1001–1014. (c) Chu, C. W.; Ouyang, J.; Tseng, H. H.; Yang, Y. Adv. Mater. 2005, 17, 1440–1443. (d) Ling, Q. D.; Chang, F. C.; Song, Y.; Zhu, C. X.; Liaw, D. J.; Chan, D. S. H.; Kang, E. T.; Neoh, K. G. J. Am. Chem. Soc. 2006, 128, 8732–8733. (e) Ling, Q. D.; Song, Y.; Lim, S. L.; Teo, E. Y. H.; Tan, Y. P.; Zhu, C. X.; Chan, D. S. H.; Kwong, D. L.; Kang, E. T.; Neoh, K. G. Angew. Chem., Int. Ed. 2006, 45, 2947–2951.

⁽³⁶⁾ Choi, D. H.; Lee, D.; Sim, H.; Chang, M.; Hwang, H. S. *Appl. Phys. Lett.* **2006**, *88*, 082904/1–082904/3.

 ^{(37) (}a) Prakash, A.; Ouyang, J.; Lin, J. L.; Yang, Y. J. Appl. Phys. 2006, 100, 054309/1–054309/4. (b) Lin, J.; Zheng, M.; Chen, J.; Gao, X.; Ma, D. Inorg. Chem. 2007, 46, 341–344. (c) Ouyang, J. Y.; Chu, C. W.; Szmanda, C. R.; Ma, L. P.; Yang, Y. Nat. Mater. 2004, 3, 918–922.



Figure 6. HOMO and LUMO energy levels of polymer 6, work functions of Al, ITO (before and after plasma treatments), and possible electric field induced hole migration process between polymer and electrodes.



Figure 7. I-V characteristics of the ITO/polymer 6/Al device in the ON and OFF states.

memory effects. The data retention ability tests were carried out on the devices in the ON- and OFF-states by applying a reading voltage of 1 V. As shown in Figure 5, the currents in both ON and OFF states did not show any degradation, suggesting good device stability. The ON/OFF current ratio observed in the sweep I-V characteristics at +1.0 V is 6.1×10^3 .

From Figure 6, one can clearly see that, for the positive sweep (ITO was used as cathode and Al as anode), the energy barriers of Al/polymer 6 (LUMO) and polymer 6 (HOMO)/ITO interfaces are 0.86 and 0.84 eV, respectively. While for the negative sweep (in this case the ITO was used as anode and Al as cathode), the energy barriers of ITO/polymer 6 (LUMO) and polymer 6 (HOMO)/Al interfaces are 1.38 and 1.36 eV, respectively. The high energy barriers prevent switching from the OFF state to the ON state during the negative sweep. On the other hand, hole injection would be more favorable during the positive sweep because of the electron-withdrawing effect of the abundant cyano moieties in the polymer structure. Under a low sweeping voltage sweep($0 \rightarrow 2.2$ V), the holes injection from ITO to the active polymer layer is easier, resulting in the formation of the high current state. However, when the sweeping voltage continues to increase and exceed the energy barrier, the hole migration would be destructed, and consequently the hole injection is rather difficult, giving rise to an abrupt current decrease. This phenomenon is irreversible, which implies that the low OFF state will be retained permanently in the subsequent voltage sweeps.

To further explain the conduction mechanism through ITO/polymer 6/Al device, we analyzed the I-V curves in the ON and OFF states respectively. As depicted in Figure 7, a straight line with slope of 1 is observed in the ON state, indicating that the current is Ohmic conduction.³⁹ On the other hand, the I-V characteristic shows a slope of 2 in the OFF state, implying that the Space Charge Limited Currents (SCLC) is probably the main conduction mechanism.⁴⁰ Under a low positive bias voltage ($0 \rightarrow 2.2$ V), the continuous hole injection makes the hole transport and linear conductivity more effective. While this hole injection process goes ahead, the positive charges on the TPA moieties will rapidly be consumed by cyano groups as a result of the switching operation $(ON \rightarrow OFF)$. Hence, the device maintains the OFF state during the subsequent operation. In a typical low conduction state (5 \rightarrow 0 V), the SCLC model was found to suitably fit the logarithmic plot of the I-V data of the OFF state. These results may suggest that the generated carriers lead to an accumulation of space charges and a redistribution of electric field after the ON state to OFF state transit.⁴¹ The stable charge transfer complex of the polymer 6 was formed⁴² after these operation. As the reverse bias voltage is applied (ITO as anode), the low conduction state was thus holding throughout the process, and the same phenomena occurred in the next sweeping cycles.

As we have noted previously, in the work of Williams and his co-workers at Hewlett-Packard,^{43–49} they definitively established that such devices involve metal filaments that can be formed reversibly.^{43,44} This seems to imply that it is doubtful that anyone is going to follow this work to make a real memory device. Indeed, nobody can completely avoid the possibility of metal filaments. But from our results one can clearly see that in our devices metal filaments should not be the main mechanism, as described in our text. Although 50-nm-thick polymer film

- (39) Teo, E. Y. H.; Ling, Q. D.; Song, Y.; Tan, Y. P.; Wang, W.; Kang, E. T.; Chan, D. S. H.; Zhu, C. X. Org. Electron. 2006, 7, 173–180.
- (40) Lampert, M. A.; Mark, P. Current injection in solids, Academic Press: New York, 1970.
- (41) (a) Lee, T. J.; Chang, C. W.; Hahm, S. G.; Kim, K.; Park, S.; Kim, D. M.; Kim, J.; Kwon, W. S.; Liou, G. S.; Ree, M. Nanotechnology **2009**, 20, 135204–135210. (b) Yun, D. Y.; Kwak, J. K.; Jung, J. H.; Kim, T. W.; Son, D. I. Appl. Phys. Lett. **2009**, 95, 143301/1–143301/3.
- (42) (a) Naka, K.; Uemura, T.; Chujo, Y. *Polym. J.* 2000, *32*, 435–439.
 (b) Benson-Smith, J. J.; Goris, L.; Vandewal, K.; Haenen, K.; Manca, J. V.; Vanderzande, D.; Bradley, D. D. C.; Nelson, J. *Adv. Funct. Mater.* 2007, *17*, 451–457.
- (43) Maitani, M. M.; Allara, D. L.; Ohlberg, D. A. A.; Li, Z.; Williams, R. S.; Stewart, D. R. Appl. Phys. Lett. 2010, 96, 173109/1– 173109/3.
- (44) Lau, C. N.; Stewart, D. R.; Williams, R. S.; Bockrath, M. *Nano Lett.* 2004, *4*, 569–572.
 (45) Borghetti, J.; Snider, G. S.; Kuekes, P. J.; Yang, J. J.; Stewart,
- (45) Borghetti, J.; Snider, G. S.; Kuekes, P. J.; Yang, J. J.; Stewart D. R.; Williams, R. S. *Nature* **2010**, *464*, 873–876.
- (46) Yang, J. J.; Borghetti, J.; Murphy, D.; Stewart, D. R.; Williams, R. S. Adv. Mater. 2009, 21, 3754–3758.
- (47) Yang, J. J.; Pickett, M. D.; Li, X. M.; Ohlberg, D. A. A.; Stewart, D. R.; Williams, R. S. Nat. Nanotechnol. 2008, 3, 429–433.
- (48) Borghetti, J.; Li, Z. Y.; Straznicky, J.; Li, X. M.; Ohlberg, D. A. A.; Wu, W.; Stewart, D. R.; Williams, R. S. Proc. Natl. Acad. Sci. U.S. A. 2009, 106, 1699–1703.
- (49) Strukov, D. B.; Williams, R. S. Proc. Natl. Acad. Sci. U.S.A. 2009, 106, 20155–20158.

may have pinholes, but if so, the device would not be able to work normally. In our experiment, the polymer can form uniform good film without pinholes, which means that the short circuits seem impossible after evaporating Al. As a result, we did not observe the short circuits during the measurements. We tested many devices to test this. As expected, all the results were similar.

Conclusions

The facile functionalization at the C-9 position of the fluorene unit may offer an opportunity to reduce the interchain interactions thereby improving the electric, optoelectronic, and photonic properties of the resulting polymers. In this study, a highly soluble polyfluorene-based copolymer was prepared by reaction of 9,9-bis[3,4-bis(3,4dicyanophenoxy)phenyl]-2,7-dibromo-9*H*-fluorene with 9,9bis(4- diphenylaminophenyl)-2,7-dibromofluorene under Yamamoto-coupling conditions. The content of the cyano groups in the polymer structure can be easily controlled by adjusting the monomer levels used for polymerization. This material has a number average molecular weight (M_n) of 1.1×10^4 , with a polydispersity of 4.4, and exhibits strong photoluminescence with maximum emission peaks centered at 413 and 433(sh) nm in chloroform. The observed larger Stokes shift for the sample is associated with a substantial change of the geometric structure from the ground state (S₀) to the first excited state (S₁) as a result of an ICT or excited-state proton transfer. The estimated HOMO, LUMO, energy bandgap, ionization potential, and electron affinity were -5.66, -3.44, 2.22, 5.92, and 3.70 eV, respectively. The as-fabricated polymer film exhibited typical stable WORM memory characteristics, with long retention time of more than 3000 s without any degradation and high ON/OFF ratio of 6×10^3 . The conduction mechanism through ITO/polymer/Al device was discussed in detail.

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