Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2014

Supporting Information

Effect of Side-Chain and Linkage-Mediated Anthraquinone Moiety on Ambipolar Poly(triphenylamine)-based Volatile Polymeric Memory Devices

By Jia-Hao Wu, Hung-Ju Yen, Yi-Cheng Hu, and Guey-Sheng Liou*

Functional Polymeric Materials Laboratory, Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan Tel: +886-2-336-5315; Fax: +886-2-336-5237; E-mail: <u>gsliou@ntu.edu.tw</u>

List of Contents for Supplementary Material:

Materials	<u>SI-2</u>
Monomer Synthesis	<u>SI-2</u>
Polymer Synthesis	<u>SI-3</u>
Measurements	<u>SI-4</u>
Fabrication and Measurement of the Memory Device	<u>SI-4</u>
Scheme S1. Synthesis route to target compound 3 and 4.	<u>SI-6</u>
Scheme S2. Preparation procedure of PTPA, PTPA-AQ, and PTPA-OAQ	<u>SI-7</u>
Scheme S3. Postulated redox chemistry of anthrquinone moiety	<u>SI-8</u>
Figure S1. IR spectra of (a) compound 3 and (b) compound 4.	<u>SI-9</u>
Figure S2. (a) ¹ H NMR and (b) ¹³ C NMR spectra of compound 3 in CDCl ₃	<u>SI-10</u>
Figure S3. (a) COSY and (b) HSQC spectra of compound 3 in CDCl ₃	<u>SI-11</u>
Figure S4. (a) ¹ H NMR and (b) ¹³ C NMR spectra of compound 4 in CDCl ₃	<u>SI-12</u>
Figure S5. (a) COSY and (b) HSQC spectra of compound 4 in CDCl ₃	<u>SI-13</u>
Figure S6. ¹ H NMR spectra of (a) PTPA-AQ and (b) PTPA-OAQ in CDCl ₃	<u>SI-14</u>
Figure S7. TGA thermograms of PTPA, PTPA-AQ, and PTPA-OAQ	<u>SI-15</u>
Figure S8. DSC thermograms of PTPA, PTPA-AQ, and PTPA-OAQ	<u>SI-16</u>
Figure S9. Cyclic voltammetric diagrams of PTPA, PTPA-AQ, and PTPA-OAQ f	ilms. <u><i>SI-17</i></u>
Figure S10. Retention time test of PTPA-OAQ memory device.	<u>SI-18</u>
Figure S11. Writing/Reading cycle test of PTPA-OAQ memory device	<u>SI-19</u>
Table S1. Inherent viscosity and molecular weights of studied materials	<u>SI-20</u>
Table S2. Thermal properties of obtained polymers	<u>SI-21</u>

Materials

4-Methoxytriphenylamine¹ (1) and 4-hydroxytriphenylamine² (2) were prepared according to the literatures. Tetrabutylammonium perchlorate (TBAP) (ACROS) was recrystallized twice by ethyl acetate under nitrogen atmosphere and then dried *in vacuo* prior to use. All other reagents were used as received from commercial sources.

Monomer Synthesis

2-diphenylaminoanthracene-9,10-dione (3)



In a 250 mL three-neck round-bottom flask equipped with a stirring bar in a nitrogen atmosphere, 6.69 g (30.00 mmol) 2-amino-anthraquinone, 15.30 g (75.00 mmol) of iodobenzene, 10.36 g (75.00 mmol) potassium carbonate, 4.82 g (75.00 mmol) copper, and 1.99 g (7.53 mmol) of 18-crown-6-ether were stirred in 30 mL o-dichlorobenzene at 180 °C for 27 h in a nitrogen atmosphere. The inorganic salt was removed by filtration of the hot reaction mixture, and the product was precipitated into 150 mL of stirred methanol. The precipitated brown powders was dissolved in toluene and filtrated for removing copper. The product was collected by concentration to afford 8.39 g (74.5 % in yield) of brown powders. Mp: 190-193 °C measured by DSC at a scan rate of 10 °C/ min. IR (KBr): 1674 cm⁻¹ (C=O stretch). ¹H NMR (500 MHz, CDCl₃, δ, ppm): 8.26-8.24 (d, 1H, H_g), 8.19-8.17 (d, 1H, H_d), 8.09-8.07 (d, 1H, H_c), 7.75-7.74 (d, H, H_a), 7.73-7.67 (m, 2H, H_e + H_f), 7.36-7.33 (t, 4H, H_i), 7.24-7.22 (dd, 1H, H_b), 7.20-7.14 (m, 6H, H_b + H_i). ¹³C NMR (125MHz, CDCl₃, δ , ppm): 183.37 (C¹³), 181.55 (C⁶), 152.99 (C²), 145.72 (C¹⁵), 134.86 (C¹⁴), 133.95 (C¹⁰), 133.93 (C¹²), 133.52 (C⁷), 133.30 (C⁹), 129.85 (C¹⁷), 129.12 (C⁴), 126.93 (C⁸), 126.91 (C¹¹), 126.27 (C¹⁶), 125.71 (C⁵), 125.45 (C¹⁸), 123.73 (C³), 116.37 (C¹). Anal. Calcd. (%) for C₂₆H₁₇NO₂ (375.42): C, 83.18; H, 4.56; N, 3.73. Found: C, 83.21; H, 4.46; N, 3.70.

2-(4-diphenylaminophenoxy)anthracene-9,10-dione (4)



A mixture of 3.18 g (23.00 mmol) of potassium carbonate in 40 mL dimethyl sulfoxide (DMSO) was stirred at room temperature. To the mixture 3.82 g (15.70 mmol) of 2chloroanthracene-9,10-dione and 3.96 g (15.00 mmol) of 2 were added in sequence. The mixture was heated with stirring at 120 °C for 20 h and slowly poured into 300 mL methanol/water (2:1). The product was purified by THF/ methanol to afford 5.56g (79.3 % in yield) of yellow powders with a mp of 177–179 °C (by Melting Point System at a scan rate of 5°C /min). FT-IR (KBr): 1672 cm⁻¹ (C=O stretch) and 1213 cm⁻¹ (C=O stretch). ¹H NMR $(500 \text{ MHz}, \text{ CDCl}_3, \delta, \text{ ppm})$: 8.30-8.27 (d, 1H, H_c), 8.27-8.25 (m, 2H, H_d + H_g), 7.80-7.78 (d,1H, H_a), 7.77-7.74 (m, 2H, H_e+ H_f), 7.36-7.34 (dd, 1H, H_b), 7.27-7.24 (dd, 4H, H_k), 7.14-7.11 (m, 6H, $H_h + H_i$), 7.03-6.96 (m, 6H, $H_i + H_i$). ¹³C NMR (125MHz, CDCl₃, δ , ppm): 182.93 (C¹³), 182.09 (C⁶), 163.40 (C²), 149.69 (C¹⁵), 147.871 (C¹⁹), 145.22 (C¹⁸), 135.68 (C¹⁴), 134.25 (C⁹), 133.84 (C¹⁰), 133.62 (C⁷), 133.59 (C¹²), 130.07 (C⁴), 129.37 (C²¹), 128.20 (C⁵), 127.23 (C⁸), 127.20 (C¹¹), 125.49 (C¹⁶), 124.22 (C²⁰), 122.98 (C²²), 122.73 (C³), 121.32 (C¹⁷), 114.21 (C¹). Anal. Calcd (%) for C₃₂H₂₁NO₃ (467.51): C, 82.21; H, 4.53; N, 3.00. Found: C, 81.87; H, 4.31; N, 2.62. ESI-MS: calcd for (C₃₂H₂₁NO₃)⁺: m/z 467.5; found: m/z 468.2.

Polymer Synthesis

The oxidative coupling reaction was used to synthesize the studying materials according to the previous literature.¹ **PTPA-OAQ** was chosen as an example to illustrate the general synthetic route of the oxidative coupling reaction. To a two-necked 50 mL flask equipped with a magnetic stirrer were placed 2-(4-diphenylaminophenoxy)anthracene-9,10-dione (1 mmol) and chloroform (3 mL) under nitrogen atmosphere. A quarter portion of FeCl₃ (1 mmol; total is 4 mmol) was added to the reaction mixture at the interval of 1 h. The solution was stirred at 45 °C for 48 h then poured into a mixture of methanol containing 10%

hydrochloric acid to recover the product. Collected powder was washed in dilute ammonia aqueous solution. The resulting polymer was filtrated and dried in vacuo at 120 °C for 12 h (yield: 94%).

Measurements

Elemental analysis was run in a elementar Vario EL cube elemental analyzer. The inherent viscosities were determined at 0.5 g/dL concentration using Tamson TV-2000 viscometer at 30 °C. Gel permeation chromatographic (GPC) analysis was carried out on a Waters chromatography unit interfaced with a Waters 2410 refractive index detector. Two Waters 5 μ m Styragel HR-2 and HR-4 columns (7.8 mm I. D. \times 300 mm) were connected in series with NMP as the eluent at a flow rate of 0.5 ml/min at 40 °C and were calibrated with polystyrene standards. DSC analyses were performed on a TA Instruments Q20 in flowing nitrogen (50 cm³/min) at a heating rate of 20 °C/min. Thermogravimetric analysis (TGA) was conducted with a TA Instruments Q50 in flowing nitrogen or air (flow rate = $60 \text{ cm}^3/\text{min}$) at a heating rate of 20 °C/min. Cyclic voltammetry (CV) was performed with a CH Instruments 611B electrochemical analyzer and conducted with the use of a three-electrode cell in which ITO (polymer films area about 0.5 cm x 1.2 cm) was used as a working electrode and a platinum wire as an auxiliary electrode at a scan rate of 100 mV/s against a Ag/AgCl reference electrode in anhydrous DMF and CH₃CN, using 0.1 M of TBAP as a supporting electrolyte in nitrogen atmosphere. All cell potentials were taken by using a homemade Ag/AgCl, KCl (sat.) reference electrode. The ITO-coated glass slide was used as the working electrode, a platinum wire as the counter electrode, and a Ag/AgCl cell as the reference electrode. Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer Spectrum 100 Model FT-IR spectrometer. NMR spectra were measured on a Bruker AVIII-500MHz FT-NMR in CDCl₃. Photoluminescence (PL) spectra was measured with HORIBA Fluorolog-3 spectrofluorometer.

Fabrication and Measurement of the Memory Device

The ITO glass used for memory device was precleaned by ultrasonication with water, acetone, and isopropanol each for 15 min. The solution of **PTPA-AQ** or **PTPA-OAQ** (5 mg/mL in chloroform) was filtered through 0.45 μ m pore size of PTFE membrane syringe filter. Then, 250 μ L of the filtered solution was spin-coated onto the ITO glass at a rotation rate of 1000

rpm for 60 s and kept at 70 °C for 10 min under nitrogen. The film thickness was determined to be around 50 nm. Finally, a 300-nm-thick Al top electrode was thermally evaporated through the shadow mask (recorded device units of 0.5×0.5 mm² in size) at a pressure of 10^{-7} torr with a uniform depositing rate of 3-5 Å/s. The electrical characterization of the memory device was performed by a Keithley 4200-SCS semiconductor parameter analyzer equipped with a Keithely 4205-PG2 arbitrary waveform pulse generator. ITO was used as common electrode and Al was the electrode for applying voltage during the sweep. The probe tip used 10 µm diameter tungsten wire attached to a tinned copper shaft with a point radius < 0.1 µm (GGB Industries, Inc.).

Molecular Simulation

The Molecular simulation in this study was performed by Gaussian 09 program package. The results of value and distributions of the corresponding energy levels within each basic unit of **PTPA-AQ** and **PTPA-OAQ** were investigated via density functional theory (DFT) method at the B3LYP level of theory (Beckesstyle three-parameter density functional theory using the Lee-Yang-Parr correlation functional) with the 6-31G (d) basic set.



Scheme S1. Synthesis route to target compound 3 and 4.



Scheme S2. Preparation procedure of PTPA, PTPA-AQ, and PTPA-OAQ.



Scheme S3. Postulated redox structures of anthraquinone moiety.



Figure S1. IR spectra of (a) compound 3 and (b) compound 4.

Figure S2. (a) ¹H NMR and (b) ¹³C NMR spectra of compound 3 in CDCl₃.



Figure S3. (a) COSY and (b) HSQC spectra of compound 3 in CDCl₃.

Figure S4. (a) 1 H NMR and (b) 13 C NMR spectra of compound 4 in CDCl₃.



Figure S5. (a) COSY and (b) HSQC spectra of compound 4 in CDCl₃.



Figure S6. ¹H NMR spectra of (a) PTPA-AQ and (b) PTPA-OAQ in CDCl₃.



Figure S7. TGA thermograms of PTPA, PTPA-AQ, and PTPA-OAQ at a scan rate of 20 °C/min.



Figure S8. DSC thermograms of PTPA, PTPA-AQ, and PTPA-OAQ at a scan rate of 20 °C/min.



Figure S9. Cyclic voltammetric diagrams of **PTPA**, **PTPA-AQ**, and **PTPA-OAQ** films on an ITO-coated glass substrate over cyclic scans in 0.1 M TBAP/CH₃CN at a scan rate of 100 mV/s.



Figure S10. Retention time test of PTPA-OAQ memory device.



Figure S11. Writing/Reading cycle test of **PTPA-OAQ** memory device. (a)~(e) *I-V* diagram of each cycle; (f) summarized diagram.

Code	yield	$\eta_{inh}{}^{a} \left(dL/g \right)$	$M_w{}^b$	$M_n{}^b$	PDI ^b	Solvent ^c		
						DMAc	NMP	CHCl ₃
РТРА	88.1%	0.40	63000	40000	1.56		+	++
PTPA-AQ	79.1%	0.16	5100	2900	1.76	_	+	++
PTPA-OAQ	80.1%	0.15	4900	2700	1.81	_	+	++

Table S1. Inherent viscosity and molecular weights of studied materials

^a Measured at a polymer concentration of 0.5 g/dL in NMP at 30 °C.

^{*b*} Calibrated with polystyrene standards, using NMP as the eluent at a constant flow rate of 1 ml/min at 40 °C. Polydispersity Index (M_w/M_n) .

^{*c*} The solubility was determined with a 5 mg sample in 1 ml of solvent. ++: soluble in room temperature; +: soluble in heating; -: partially soluble even in heating.

Polymer ^a	Тg (°С) ^{<i>b</i>} –	$T_{d}^{5} (^{\circ}\mathrm{C})^{c}$		$T_{\rm d}{}^{10}$	(°C) ^c	\mathbf{D} (0/) d	I OIe
		N_2	Air	N_2	Air	$ K_{W800} (70)^{}$	LOI
РТРА	267	435	440	475	485	67	44.3
PTPA-AQ	238	505	490	540	545	68	44.7
PTPA-OAQ	186	505	505	535	540	75	47.5

Table S2. Thermal properties of obtained polymers

^a The polymer samples were heated at 200 °C for 1 h prior to all the thermal analyses.

^{*b*} The Midpoint temperature of baseline shift on the DSC heating trace at a heating rate of 20 °C /min).

^{*c*} Temperature at which 5 % and 10 % weight loss occurred, respectively, recorded by TGA at a heating rate of 20 °C/min and a gas flow rate of 20 cm³/min.

^dResidual weight percentages at 800 °C under nitrogen flow.

^{*e*}LOI = Limiting Oxygen Index = $(17.5 + 0.4 \times \text{char yield})$.³

Reference

- 1. (a) H. W. Chang, K. H. Lin, C. C. Chueh, G. S. Liou and W. C. Chen, *J. Polym. Sci.*, *Part A: Polym. Chem.*, 2009, **47**, 4037; (b) H. Y. Lin and G. S. Liou, *J. Polym. Sci.*, *Part A: Polym. Chem.*, 2009, **47**, 285.
- 2. M. Faccini, M. Balakrishnan, M. B. J. Diemeer, R. Torosantucci, A. Driessen, D. N. Reinhoudt and W. Verboom, *J. Mater. Chem.*, 2008, **18**, 5293.
- 3. D. W. van Krevelen, *Polymer*, 1975, **16**, 615.