Electronic Supplementary Information

Thermal Stable High ON/OFF Ratio Non-volatile Memory Devices Based on Poly(triphenylamine) with Pendent PCBM

By *Chih-Jung Chen, Jia-Hao Wu, 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: gsliou@ntu.edu.tw

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Experimental Section

Synthesis of TPAOPCBM

A 25 ml, two-necked round-bottomed flask was charged with PCBA (50 mg, 0.056 mmol), anhydrous o-dichlorobenzene (7 ml), 4-hydroxyltriphenylamine (14.6 mg, 0.056 mmol), and 4-dimethylaminopyridine (1.8 mg, 0.15 mmol). The solution was cooled to 0°C with an ice bath, and 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide hydrochloride (28.3 mg, 0.15 mmol) was added in one portion. After stirring at 0°C for 3 h, the ice bath was removed, and the dark brown reaction mixture was stirred at room temperature for 16 h. Afterward the residue was washed with water and dried in vacuum oven at 100 °C to obtain crude product. The crude product was dissolved in toluene, filtered through 0.45 μm pore size of PTFE membrane syringe filter, and removed solvent to obtain final product (45.4 mg, 71%). The ^{1}H NMR spectra of PCBM and the corresponding **TPAOPCBM** were used to confirm the resulting structures as shown in Fig. S1 and Fig. S2. The FT-IR spectra exhibit characteristic ester absorption bands of **TPAOPCBM** at 1754 (C=O stretch) and the carboxylic acid absorption of PCBA at 1703 (C=O stretch), respectively, as shown in Fig. S4. Anal. Calcd. (%) for **PCBA** were C, 95.08; H, 1.35; N, 0; and found C, 93.01; H, 1.45; N, 0.09. Anal. Calcd. (%) for **TPAOPCBM** were C, 93.75; H, 2.21; N, 1.23; and found C, 91.43; H, 2.27; N, 1.63.

Polymer Synthesis

The synthesis of polymer **P-TPAOPCBM10** was used as an example to illustrate the general synthetic route for **P-TPAOPCBM5** and **P-TPAOPCBM10**. To a two-necked 50 mL flask equipped with a magnetic stirrer were placed 4-methoxytriphenylamine (0.169 mmol), TPAOPCBM (0.006 mmol) and chloroform (1.5 mL) under nitrogen atmosphere. A quarter portion of $FeCl_3$ (0.175 mmol; total is 0.7 mmol) was added to the reaction mixture at the interval of 1 h. The solution was stirred at 45 °C for 24 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: 83 %). The FT-IR spectrum exhibited characteristic ester absorption bands at 1746 (C=O stretch) as shown in Fig. S4.

Fabrication and Measurement of the Memory Device

The memory device was fabricated with the configuration of ITO/thin film/Al. The ITO glass used for memory device was precleaned by ultrasonication with water, acetone, and isopropanol each for 15 min. The hybrid thin film was prepared by the chloroform solution of

polymer solutions then filtrated by 0.45 μm pore size of PTFE membrane syringe filter and spin-coated at 1000 rpm for 30 seconds onto the ITO substrate and kept at 70 ^{o}C for 10 mins 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 mm^2 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 the cathode (maintained as common), and Al was set as the anode during the voltage 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. Molecular simulations in this study were crried out with the Gaussian 09 program package. Equilibrium ground state geometry and electronic properties of basic unit of TPAOPCBM were optimized by means of the 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.

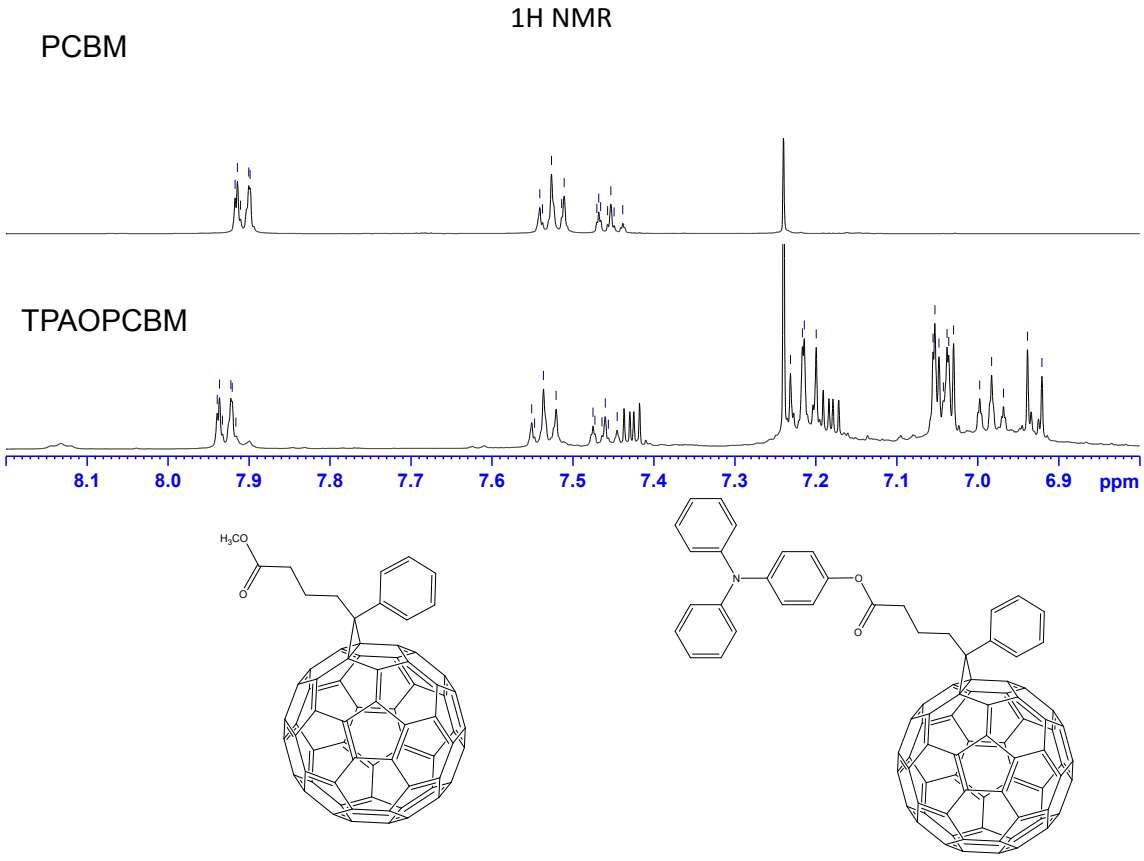

Figure S1. The ^{1}H NMR spectra of **TPAOPCBM** and corresponding PCBM.

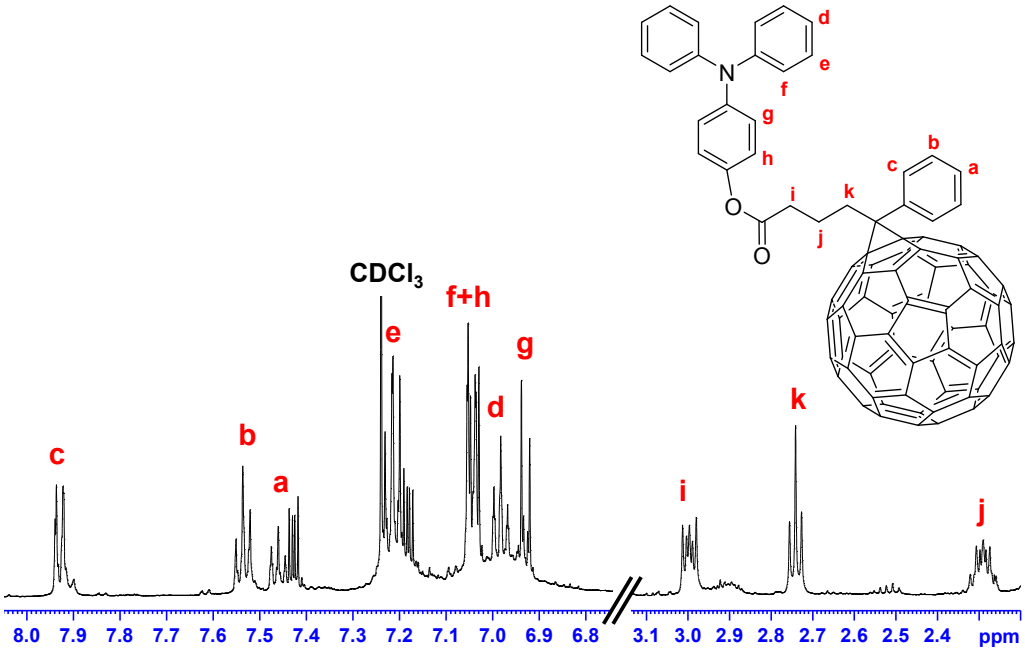

Figure S2. The ^{1}H NMR spectra of **TPAOPCBM**

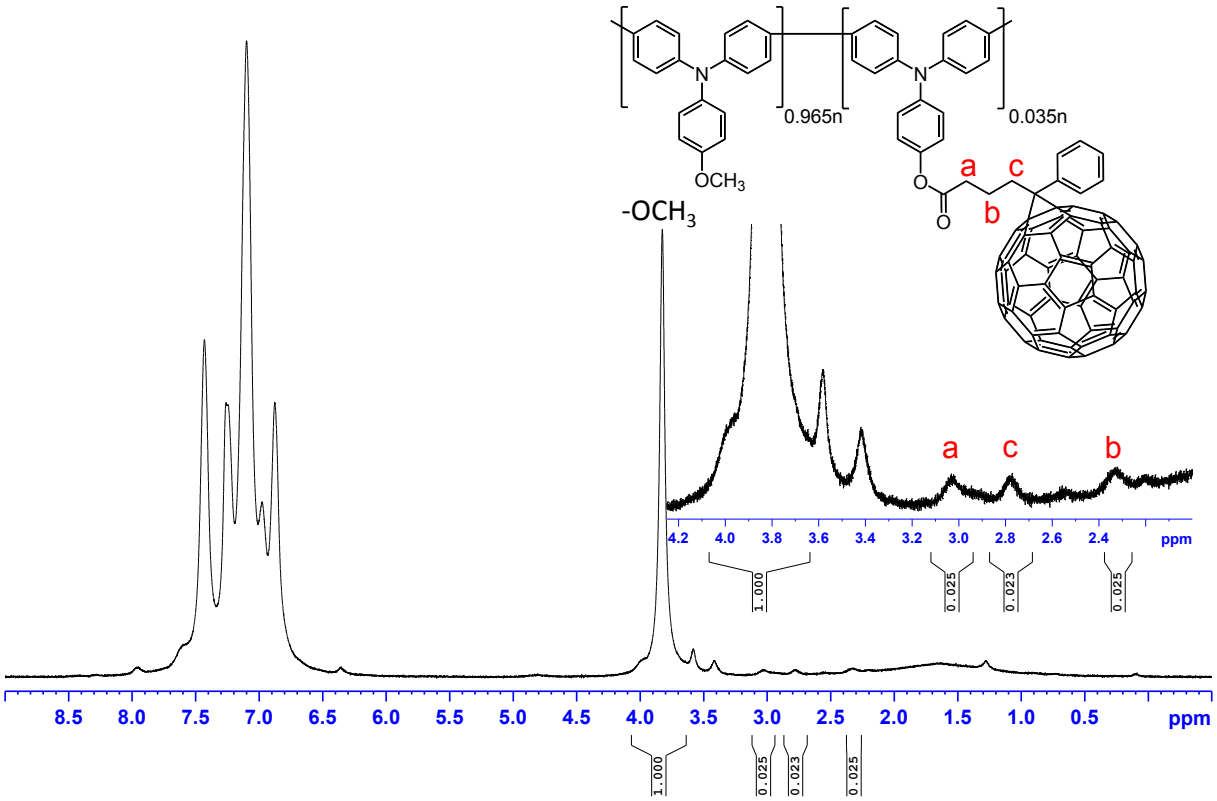

Figure S3. The ^{1}H NMR spectra of **P-TPAOPCBM10.**

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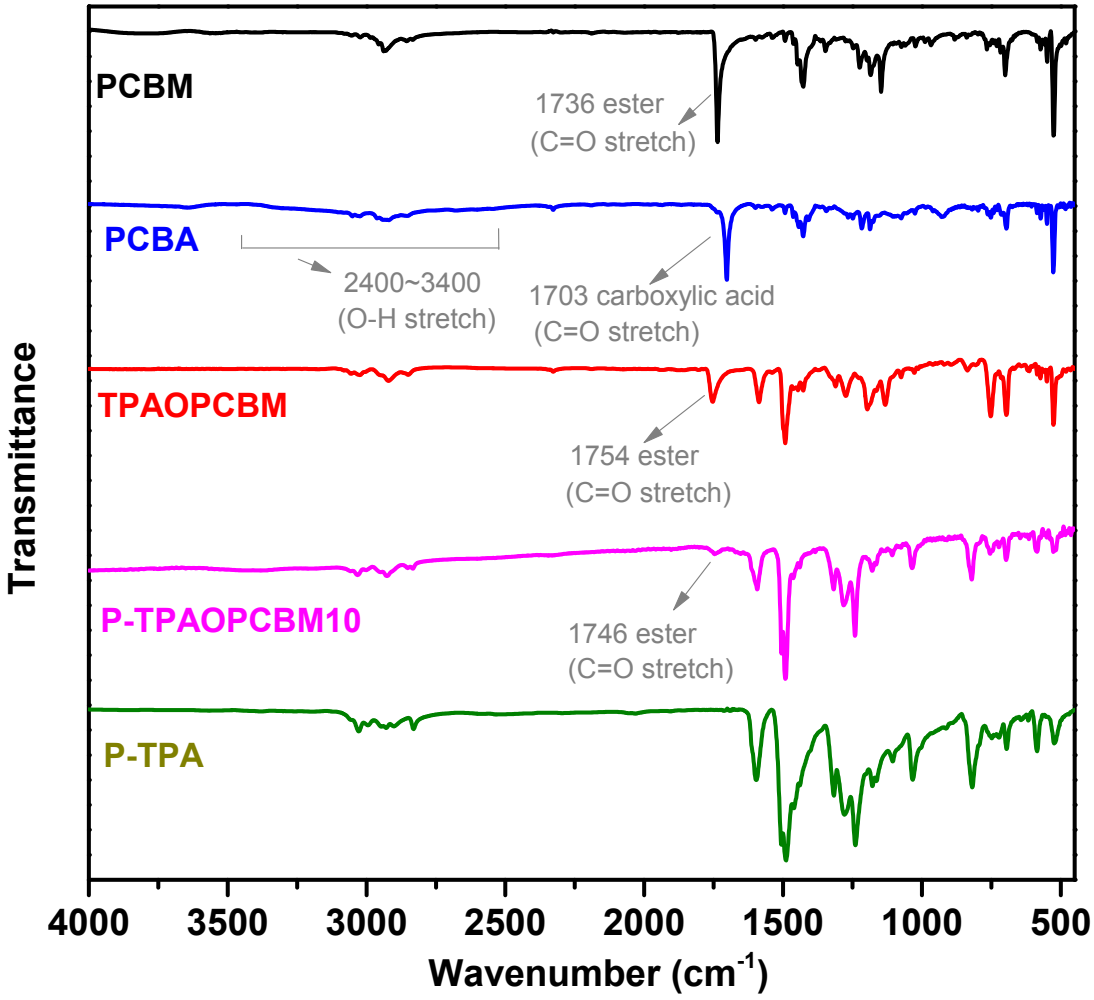

Figure S4. IR spetcra of PCBM, PCBA, TPAOPCBM, **P-TPAOPCBM10**, and **P-TPA**.

Table S1. Molecular weight of **P-TPA**.

Code	M_w	M_n	PDI
P-TPA	5800	2800	2.07

Calibrated with polystyrene standards, using NMP as the eluent at a constant flow rate of 0.5 ml/min at 40 °C. Polydispersity Index (M_w/M_n).