

### Supplementary Information

#### Iridium(III) complex-containing non-conjugated polymers for non-volatile memory induced by switchable through-space charge transfer

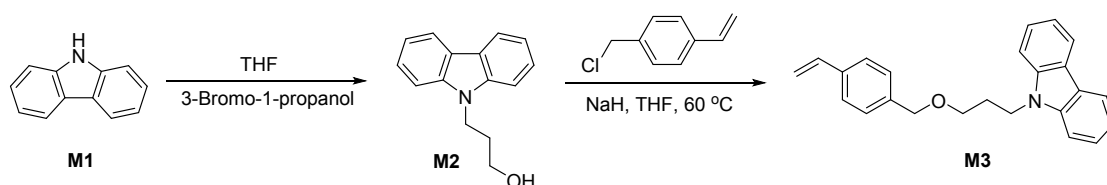
Baojie Yang<sup>†</sup>, Peng Tao<sup>†</sup>, Chenxi Ma, Runze Tang, Tao Gong, Shujuan Liu\* and Qiang Zhao\*

*Key Laboratory for Organic Electronics and Information Displays & Jiangsu Key Laboratory for Biosensors, Institute of Advanced Materials (IAM), Nanjing University of Posts and Telecommunications (NUPT), Nanjing 210023, P. R. China.*

*E-mail: iamsjliu@njupt.edu.cn; iamqzhao@njupt.edu.cn.*

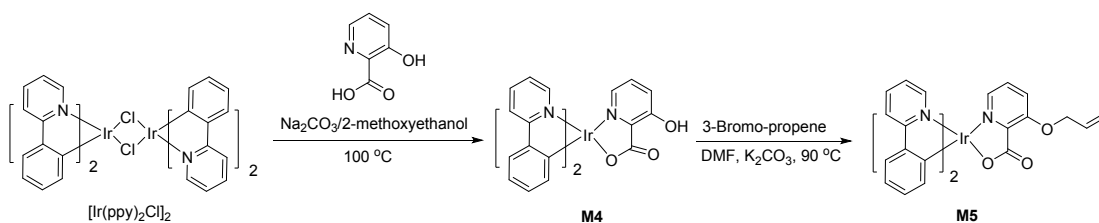
<sup>†</sup>B. Yang and P. Tao contributed equally to this work.

#### Synthesis and Characterization of Materials



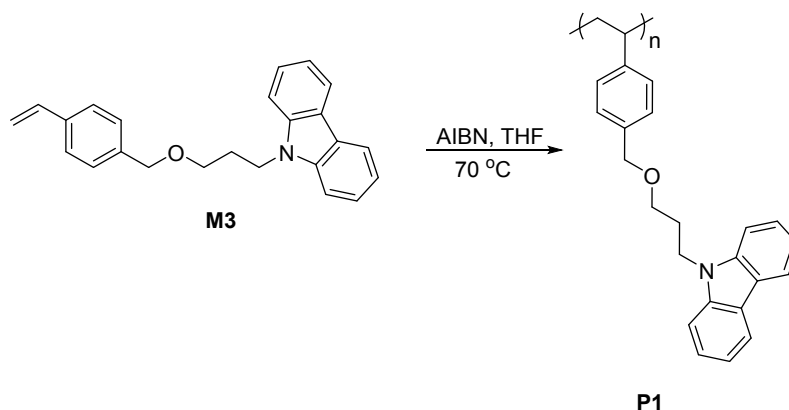
**Synthesis of monomer M2:** To the mixture of carbazole (5.0 g, 0.03 mol) and sodium hydride (2.9 g, 0.12 mol), THF (40 mL) was added. The mixture was stirred for 1 h at -15 °C. 3-bromo-1-propanol (4.0 g, 0.03 mol) was added. The mixture was stirred for 12 h at room temperature. The product was purified by column chromatography using petroleum ether and dichloromethane as the eluent to obtain bright white crystals **M2**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.11 (d, *J* = 7.6 Hz, 2H), 7.51-7.44 (m, 4H), 7.23 (m, 2H), 4.49 (t, *J* = 6.4 Hz, 2H), 3.63 (t, *J* = 5.6 Hz, 2H), 2.19-2.07 (m, 2H).

**Synthesis of monomer M3:** To the mixture of **M2** (1.5 g, 6.66 mmol), sodium hydride (0.96 g, 39.9 mmol) and THF (40 mL), 4-vinylbenzyl chloride (1.02 g, 6.70 mmol) was added. The mixture was stirred at 60 °C for 24 h under N<sub>2</sub>. The excess solvent was evaporated, and the product was extracted by diethyl ether. After concentrated, the crude product was purified by column chromatography on silica using petroleum ether: ethyl acetate=10:1(v/v) to obtain **M3** as colorless crystal with the yield of 40%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.11 (d, *J* = 8 Hz, 2H), 7.49-7.41 (m, 6H), 7.35-7.30 (m, 2H), 7.25-7.20 (m, 2H), 6.75 (dd, *J* = 17.2 Hz, 11.2 Hz, 1H), 5.78 (d, *J* = 17.2 Hz, 1H), 5.27 (d, *J* = 11.2 Hz, 1H), 4.48 (t, *J* = 6.8 Hz, 2H), 4.44 (s, 2H), 3.40 (t, *J* = 6 Hz, 1H), 2.22-2.14 (m, 2H).

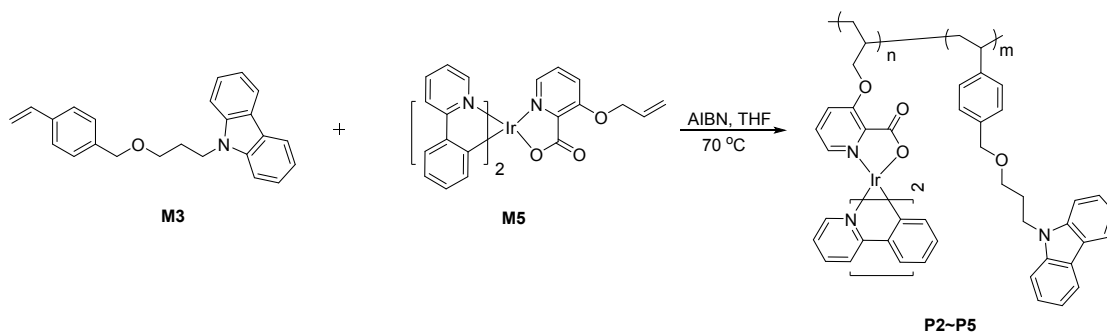


**Synthesis of  $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ :** The Ir (III) chloro-bridged dimer  $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$  was synthesized according to the previous report.<sup>[1]</sup> A solution of  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  (1 equiv) and 2-phenylpyridine (ppy, 2.5 equiv) in a mixture of 2-ethoxyethanol and water (3:1, v/v) were refluxed for 24 h. After the mixture was cooled to room temperature, excess water was added gradually to give yellow crude product. The obtained Ir (III) chloro-bridged dimer was dried under vacuum and then used for next step directly.

### Synthesis of polymer **P1**:



**Synthesis of **P1**:** To the mixture of **M3** (200 mg, 0.59 mmol) and a degassed THF (3 mL), a small amount of 2,2'-azobisisobutyronitrile (AIBN) was added as initiator. The mixture was stirred at 70 °C under  $\text{N}_2$  for 12 h. After the mixture was cooled to the room temperature, the organic phase was concentrated and then it was slowly added dropwise to a mixture of methanol and deionized water (10/1, v/v). A white fibrous solid appeared and was obtained by filtration. And this process was repeated for three times. Then, the solid was washed with acetone in a Soxhlet extractor for 3 days. Finally, we got final polymer **P1**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (brs, 3H), 7.41 (brs, 4H), 7.19-6.00 (m, 5H), 4.17 (brs, 4H), 3.54-2.84 (m, 2 H), 2.01-1.88 (m, 2H), 1.55-1.24 (m, 3H).

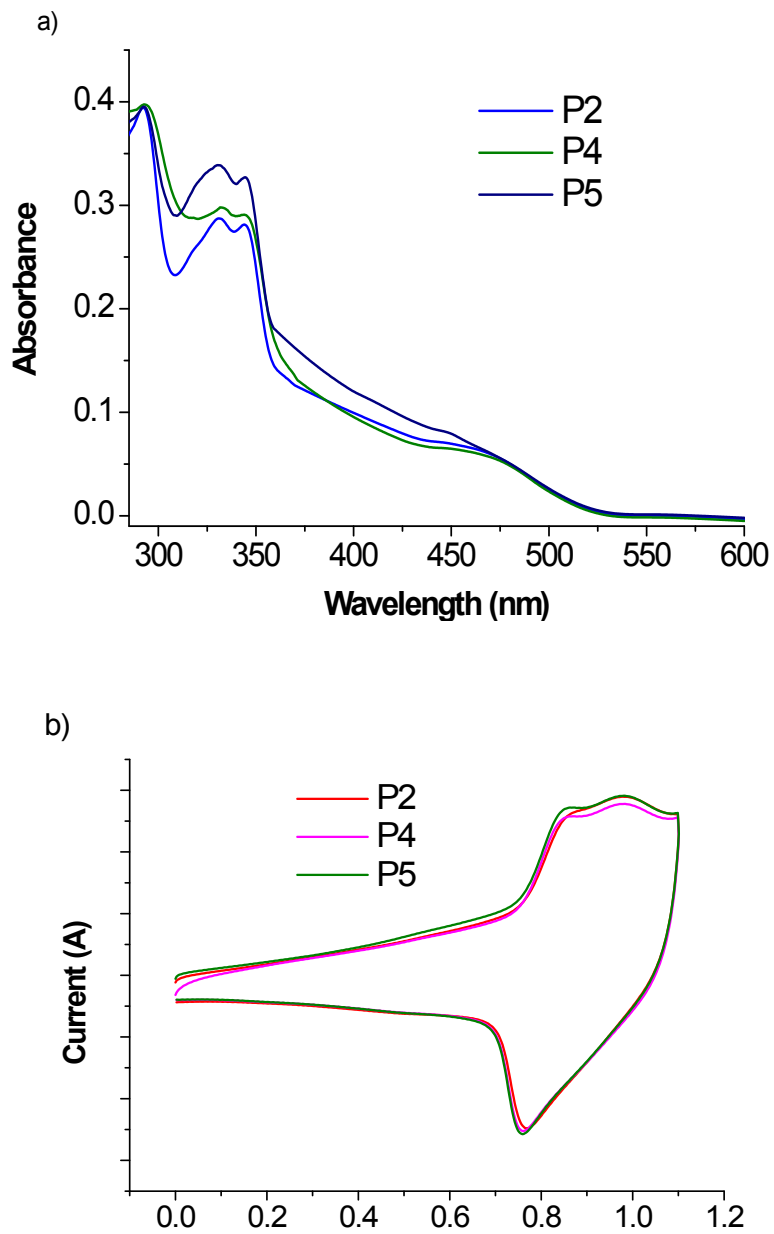


**P2:** 4%:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12-7.97 (m, 3H), 7.46-7.07 (m, 4H), 7.69-6.32 (m, 5H), 4.50-4.04 (m, 4+2\*4%H), 3.46-3.03 (m, 2H), 2.21-1.83 (d, 2H).

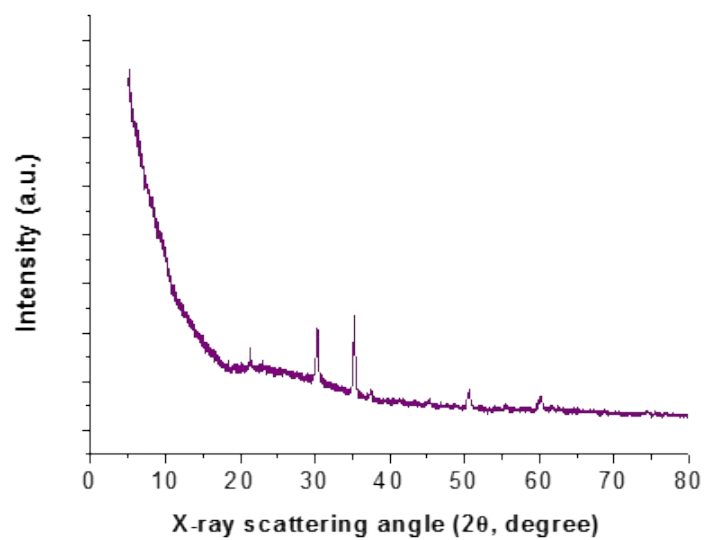
**P3:** 8%:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13-7.91 (m, 3H), 7.74-7.31 (m, 4H), 7.25-6.10 (m, 5H), 4.55-4.00 (m, 4+2\*8%H), 3.39-3.00 (m, 2H), 2.07-1.81 (m, 2H).

**P4:** 12%:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13-7.95 (m, 3H), 7.50-7.30 (m, 4H), 7.26-6.17 (m, 5H), 4.60-3.97 (m, 4+2\*12%H), 3.41-3.00 (m, 2H), 2.16-1.85 (m, 2H).

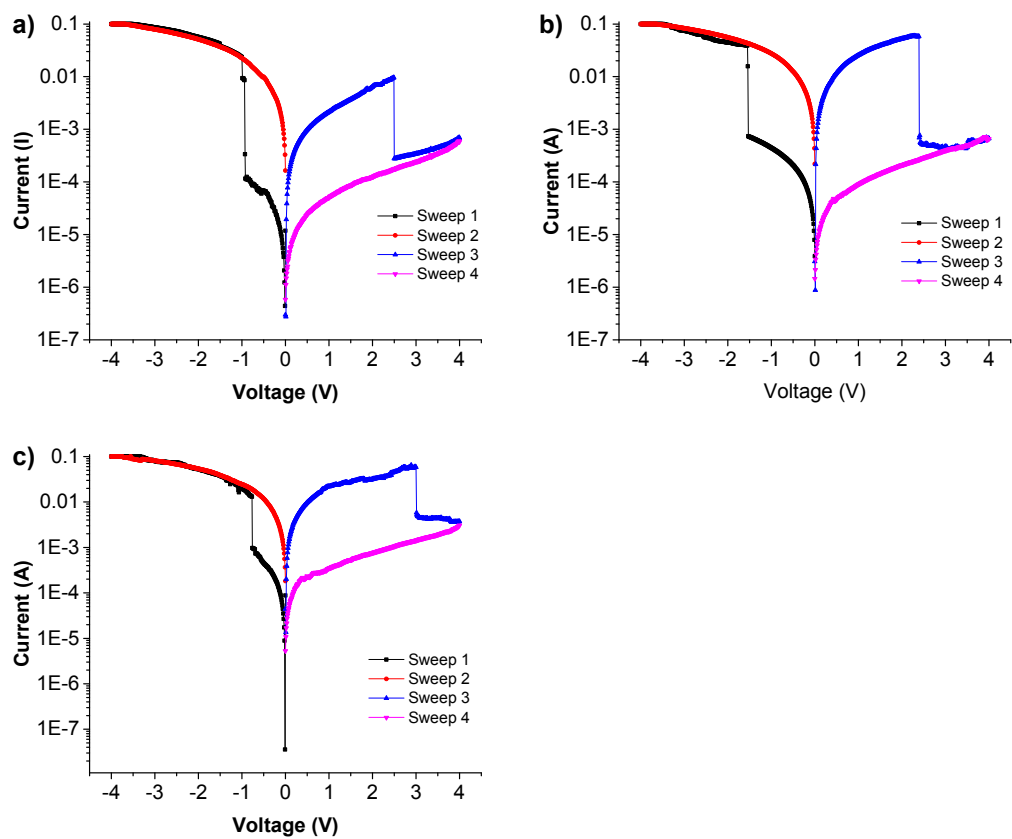
**P5:** 16%:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12-7.92 (m, 3H), 7.50-7.29 (m, 4H), 7.26-6.13 (m, 5H), 4.50-4.00 (m, 4+2\*16%H), 3.50-2.96 (m, 2H), 2.20-1.83 (m, 2H).



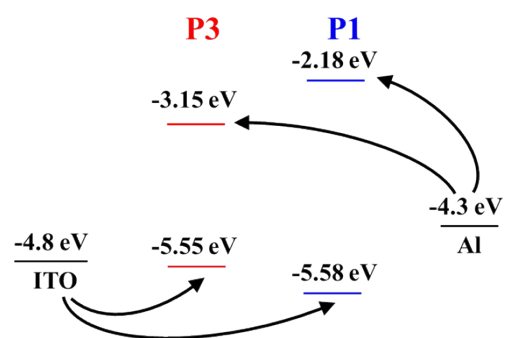
**Fig. S1** a) Absorption spectra of **P2**, **P4** and **P5** thin film on a quartz plate; b) cyclic voltammogram curves of **P2**, **P4** and **P5** with different contents of **M5** (electrolytes:  $\text{Bu}_4\text{NPF}_6$ , scanning speed: 50 mV/s).



**Fig. S2** X-ray diffraction pattern of **P3** at ground state.



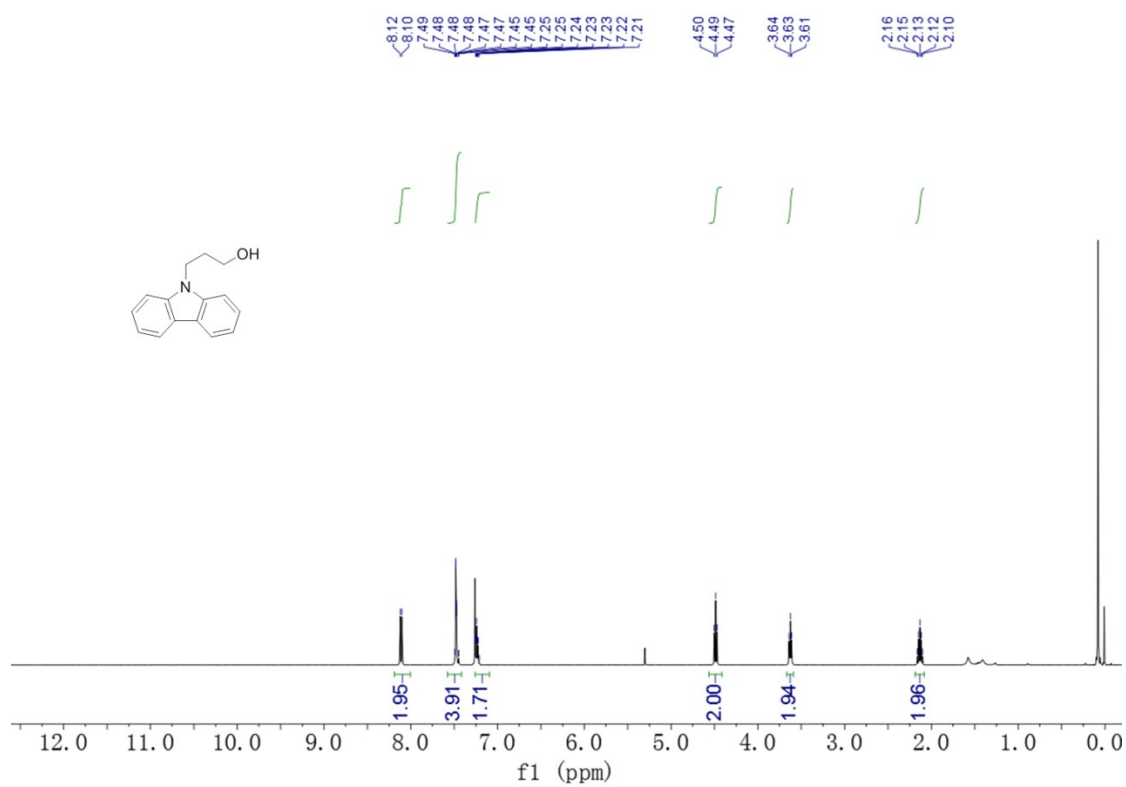
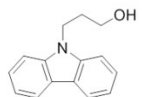
**Fig. S3**  $I-V$  characteristics of the memory devices based on polymer (a) P2, (b)P4 and (c)P5.



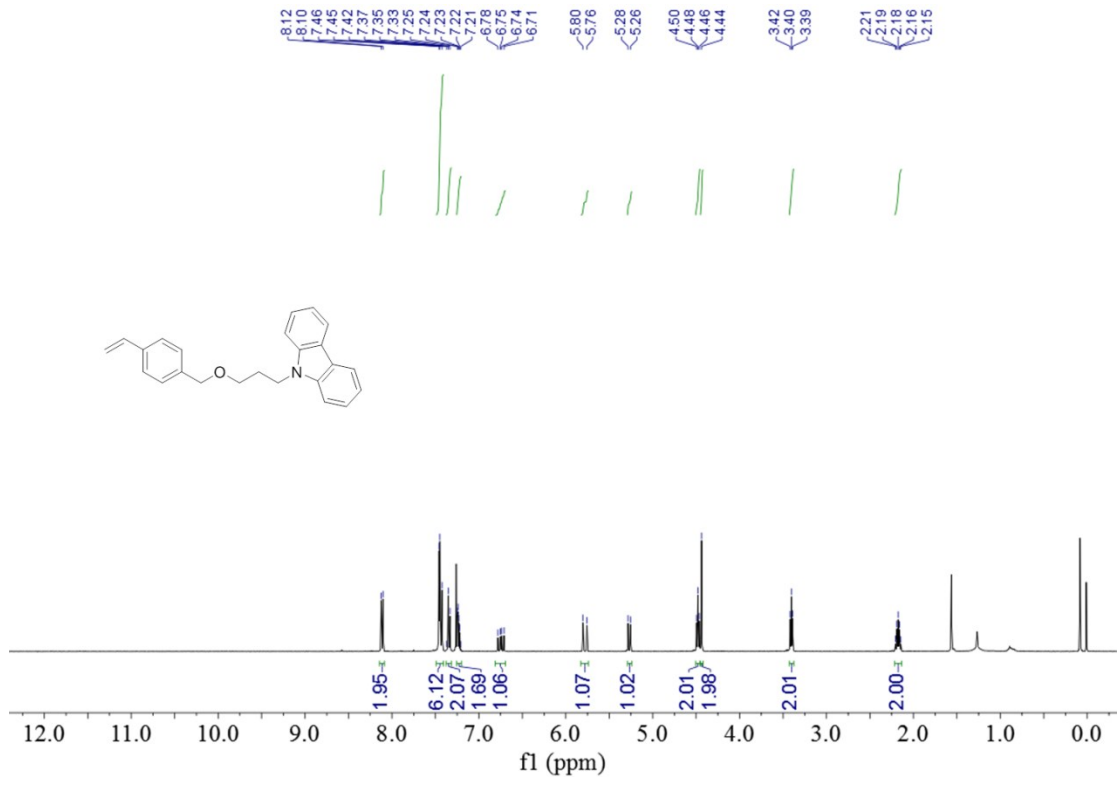
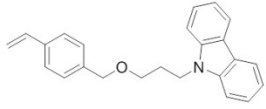
**Fig. S4** Schematic diagram of the charge injection process.

References:

- [1] K. Nonoyama, *Bull. Chem. Soc. Jpn.* **1974**, 47, 467.







—13.81

