

Supporting Information

Tunable Electrical Memory Characteristics Using Polyimides:Polycyclic Aromatic Compound Blends on Flexible Substrates

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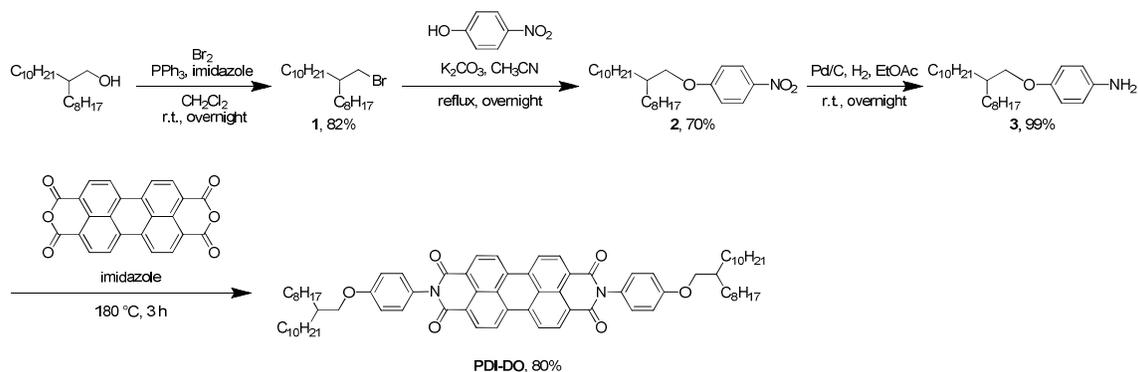
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S1. Synthesis of PDI-DO



Scheme S1. Reaction procedure for PDI-DO.

Synthesis of 2-octyl-1-bromododecane (1). To a solution of 2-octyl-1-dodecanol (5.88 g, 19.7 mmol), triphenylphosphine (6.20 g, 23.6 mmol) and imidazole (1.61 g, 23.6 mmol) in CH_2Cl_2 (40 mL) was slowly added bromine (3.78 g, 10.4 mmol) at 0°C , and the mixture was stirred at room temperature for 24 h. The reaction was then quenched with 3% $\text{Na}_2\text{S}_2\text{O}_3$ aq. The product was extracted with hexane, and then the hexane layer was washed with brine. After drying the solution over MgSO_4 followed by filtration, the filtrate was condensed under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/ CH_2Cl_2 (1/1, v/v) as an eluent to afford **1** as transparent oil (5.80 g, 82%). ^1H NMR (300 MHz, CDCl_3 , δ , ppm, 25°C): 3.44 (d, $J=3.9$ Hz, 2H, $\text{Br}-\text{CH}_2-\text{CH}$), 1.64–1.53 (m, 1H, $\text{Br}-\text{CH}_2-\text{CH}$), 1.44–1.17 (m, 32H, $-\text{CH}_2-$), 0.88 (t, $J=5.1$ Hz, 6H, $-\text{CH}_3$). ^{13}C

NMR (75 MHz, CDCl₃, δ , ppm, 25 °C): 39.89, 39.65, 32.72–26.72 (14 carbons), 22.86 (2 carbons), 14.28 (2 carbons). IR (NaCl), ν (cm⁻¹): 2924 (alkyl C—H).

Synthesis of 1-nitro-4-(2-octyldocecyl)benzene (2). The solution of compound **1** (1.25 g, 3.45 mmol), 4-nitrophenol (0.482 g, 3.46 mmol), and K₂CO₃ (0.576 g, 4.17 mmol) in CH₃CN (20 mL) was refluxed overnight under nitrogen atmosphere. After the reaction, the solution was filtered, and the filtrate was concentrated under reduced pressure. The residue was dissolved in CH₂Cl₂, washed with water, dried over MgSO₄, and the solvent was removed under reduced pressure to give a crude product, which was purified by flash silica gel column chromatography using hexane, then hexane/CH₂Cl₂ (1/1, v/v) as eluents to afford **2** as pale yellow oil (1.02 g, 70%). ¹H NMR (300 MHz, CDCl₃, δ , ppm, 25 °C): 8.18 (d, J =9.0 Hz, 2H, aromatic proton), 6.94 (d, J =9.3 Hz, 2H, aromatic proton), 3.92 (d, J =5.7 Hz, 2H, O—CH₂—), 1.90–1.73 (m, 1H, O—CH₂—CH), 1.50–1.18 (m, 32H, —CH₂—), 0.87 (t, J =6.6 Hz, 6H, —CH₃). ¹³C NMR (75 MHz, CDCl₃, δ , ppm, 25 °C): 164.60, 141.38, 125.97, 114.52, 71.88, 37.94, 32.05–26.93 (14 carbons), 22.82, 22.80, 14.23 (2 carbons). IR (NaCl), ν (cm⁻¹): 2924 (alkyl C—H), 1593, 1342 (N=O stretching).

Synthesis of 1-amino-4-(2-octyldocecyl)benzene (3). A mixture of compound **2** (0.703 g, 1.67 mmol) and Pd/C (24.0 mg, 10 wt%) in EtOAc (3 mL) was stirred at room temperature overnight under hydrogen atmosphere by using a balloon. The solution was filtered through Celite[®] and concentrated to give **3** as light brown oil (0.649 g, 99%). ¹H NMR (300 MHz,

CDCl₃, δ , ppm, 25 °C): 6.75 (d, $J=8.7$ Hz, 2H, aromatic proton), 6.64 (d, $J=8.7$ Hz, 2H, aromatic proton), 3.76 (d, $J=6.0$ Hz, 2H, O—CH₂—), 3.40 (br, 2H, —NH₂), 1.82–1.68 (m, 1H, O—CH₂—CH), 1.56–1.16 (m, 32H, —CH₂—), 0.90 (t, $J=6.3$ Hz, 6H, —CH₃). ¹³C NMR (75 MHz, CDCl₃, δ , ppm, 25 °C): 152.78, 139.84, 116.48, 115.79, 71.83, 38.19, 32.05–26.98 (14 carbons), 22.82 (2 carbons), 14.25 (2 carbons). IR (NaCl), ν (cm⁻¹): 3359, 1624 (N—H stretching), 2924 (alkyl C—H).

Synthesis of N,N-bis[4-(2-octyldodecyloxy)phenyl]-3,4,9,10-perylenetetracarboxylic diimide (4). The mixture of compound **3** (0.591 g, 1.52 mmol), 3,4,9,10-perylenetetracarboxylic dianhydride (0.199 g, 0.508 mmol), and imidazole (3.17 g) was heated at 180 °C for 3 h under argon atmosphere. Then, the reaction mixture was poured into methanol to precipitate the crude product. The product was purified by Soxhlet extraction using methanol and CHCl₃. After evaporating CHCl₃, the product was further purified by silica gel column chromatography using CH₂Cl₂ as an eluent, followed by freeze-drying from its absolute benzene solution, to afford **4** as red solid (0.462 g, 80%). ¹H NMR (300 MHz, CDCl₃, δ , ppm, 25 °C): 8.57 (d, $J=7.8$ Hz, 4H, aromatic proton), 8.32 (d, $J=8.4$ Hz, 4H, aromatic proton), 7.30 (d, $J=9.0$ Hz, 4H, aromatic proton), 7.06 (d, $J=9.0$ Hz, 4H, aromatic proton), 3.90 (d, $J=5.7$ Hz, 4H, O—CH₂—), 1.88–1.75 (m, 2H, O—CH₂—CH), 1.55–1.23 (m, 64H, —CH₂—), 0.96–0.85 (m, 12H, —CH₃). ¹³C NMR (75 MHz, CDCl₃, δ , ppm, 25 °C): 163.56, 159.70, 134.38, 131.44, 129.64, 129.38, 127.12, 126.17, 123.55,

123.15, 115.41, 71.23, 38.14, 32.09–27.04 (14 carbons), 22.85 (2 carbons), 14.29 (2 carbons). IR (KBr), ν (cm^{-1}): 2924 (alkyl C—H), 1707, 1666 (C=O stretching), 1360 (C—N stretching). MS (MALDI-TOF) m/z $[\text{M}+\text{H}^+]$: Calcd for $\text{C}_{76}\text{H}_{98}\text{N}_2\text{O}_6$, 1134.74; found, 1135.09. Anal. Calcd for $\text{C}_{76}\text{H}_{98}\text{N}_2\text{O}_6$: C, 80.38; H, 8.70; N, 2.47. Found (%): C, 80.29; H, 8.69; N, 2.45.

S2. Cyclic voltammetry of PDI-DO

Cyclic voltammetry (CV) was collected using CHI 611B electrochemical analyzer. A three-electrode cell based on ITO glass working electrode, an Ag/AgCl, KCl (sat.) reference electrode (calibrated vs Fc/Fc^+) and a Pt wire counter electrode was purged with a nitrogen. The electrochemical properties of the polymer films were detected under 0.1 M anhydrous acetonitrile solution containing tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. The highest occupied molecular orbital (HOMO) energy level, the lowest unoccupied molecular orbital (LUMO) energy level, and the electrochemical band gap (E_g^{ec}) were estimated from the onset oxidation potential ($E_{\text{onset}}^{\text{ox}}$) and onset reduction potential ($E_{\text{onset}}^{\text{red}}$), based on the following equations: $\text{HOMO} = -e[E_{\text{onset}}^{\text{ox}} - E_{1/2}^{\text{ferrocene}} + 4.8]\text{V}$; $\text{LUMO} = -e[E_{\text{onset}}^{\text{red}} - E_{1/2}^{\text{ferrocene}} + 4.8]\text{V}$, where the potential is referred to an Ag/AgCl reference electrode.

S3. Theoretical calculation

Theoretical molecular simulation of ground state structures for coronene is investigated using density functional theory (DFT) method. The B3LYP functional is used in conjunction with 6-31G(d) basis set.

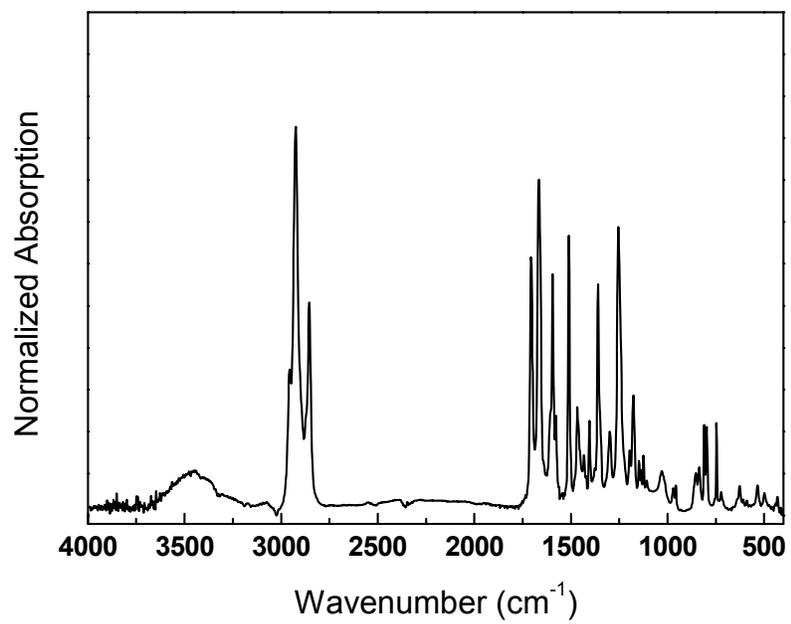


Figure S1. FT-IR spectrum of **PDI-DO**.

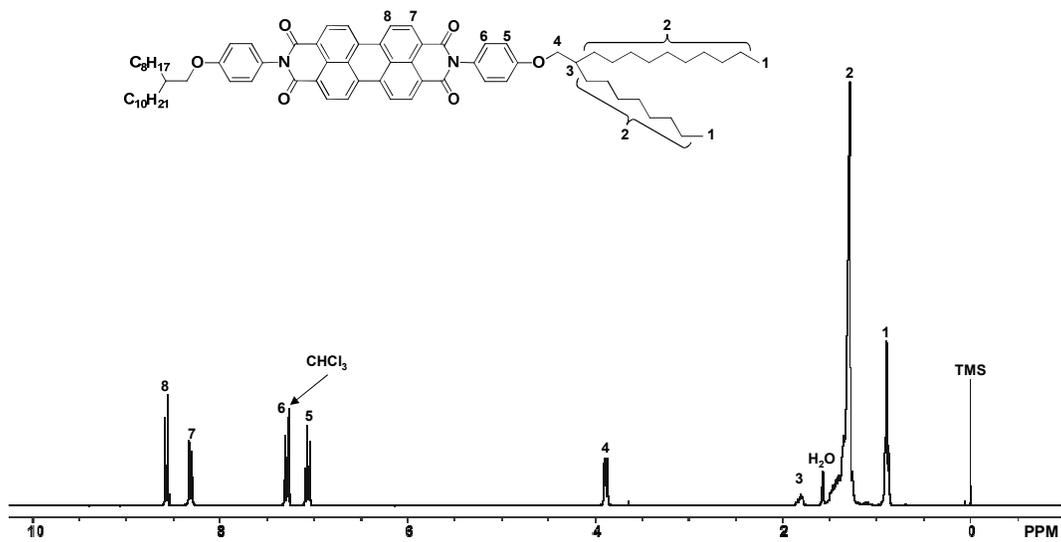


Figure S2. ¹H NMR spectrum of **PDI-DO** in CDCl₃.

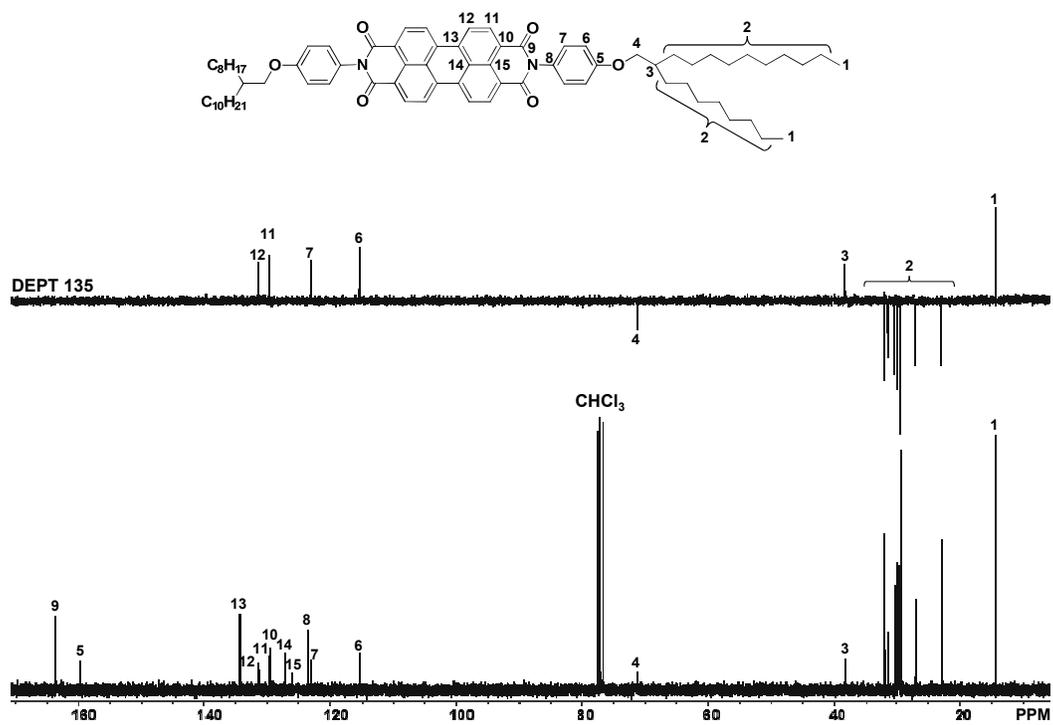


Figure S3. ^{13}C NMR spectrum of **PDI-DO**. The upper part shows the DEPT-135 spectrum.

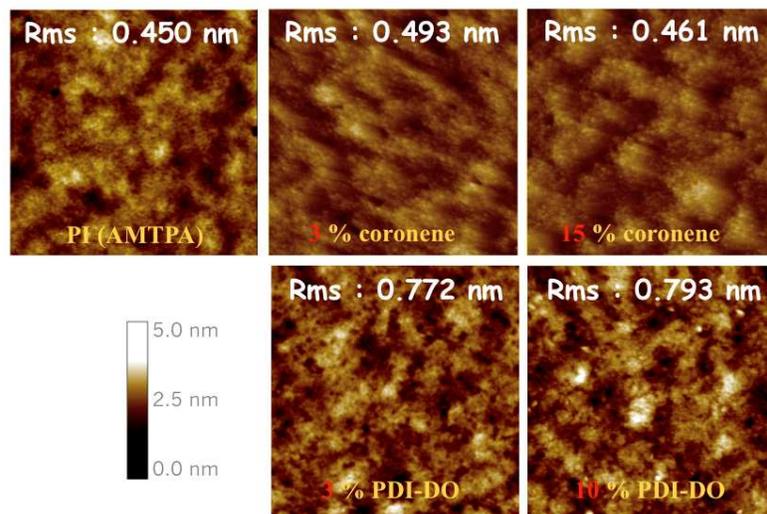


Figure S4. AFM images of **PI(AMTPA):coronene** or **PDI-DO** blend films.

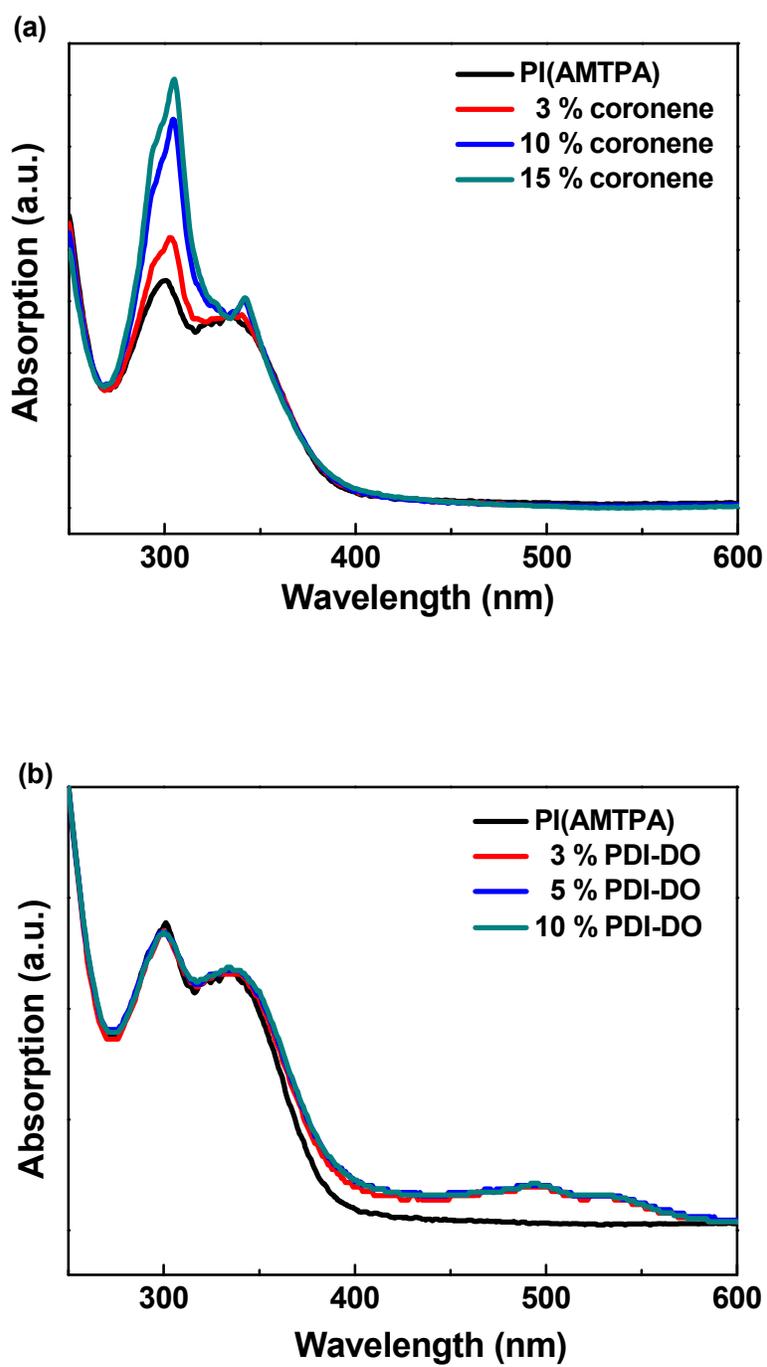


Figure S5. Absorption spectra of (a) PI(AMTPA):coronene and (b) PI(AMTPA):PDI-DO

blend thin films.

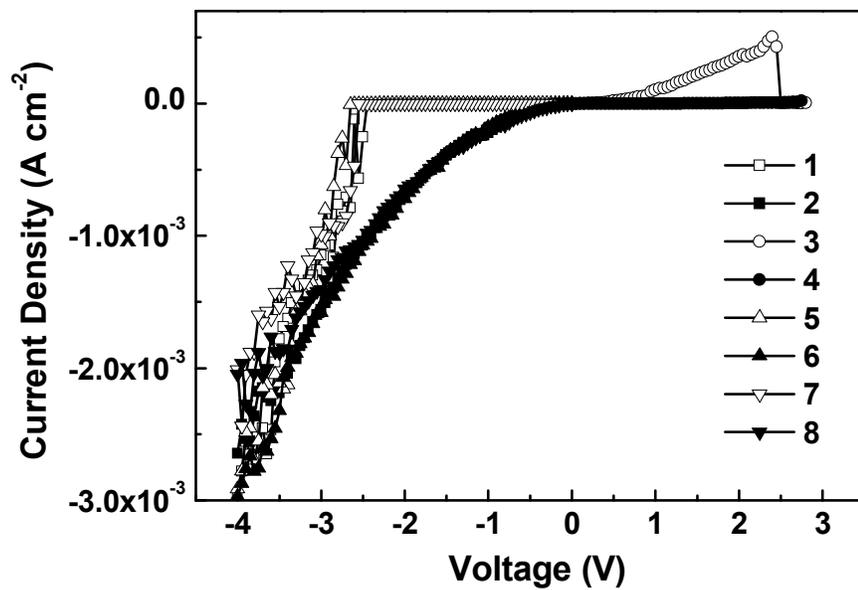


Figure S6. Current density-voltage (J - V) in linear scale of the memory device using the blend of PI(AMTPA):3% coronene.

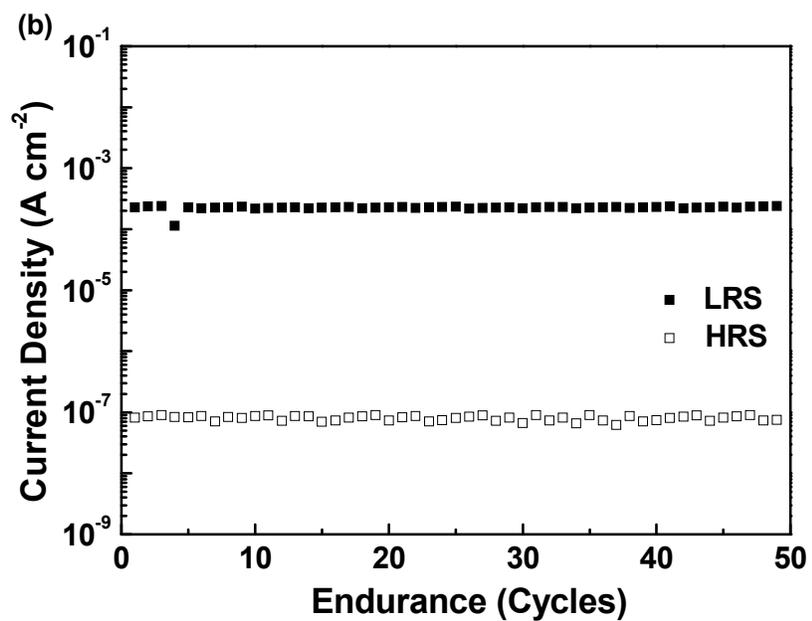
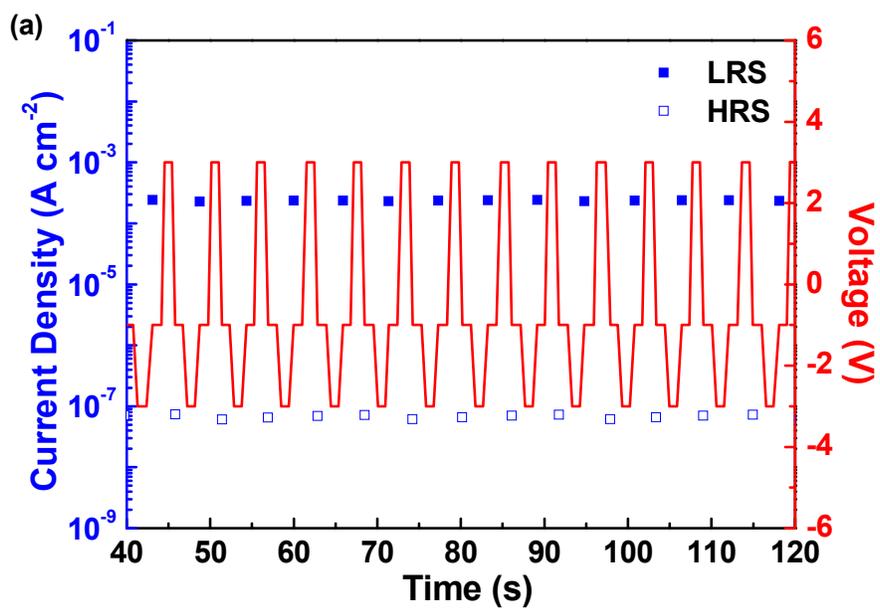


Figure S7. (a) WRER cycles and (b) endurance of the **PI(AMTPA):3% PDI:DO** memory device.

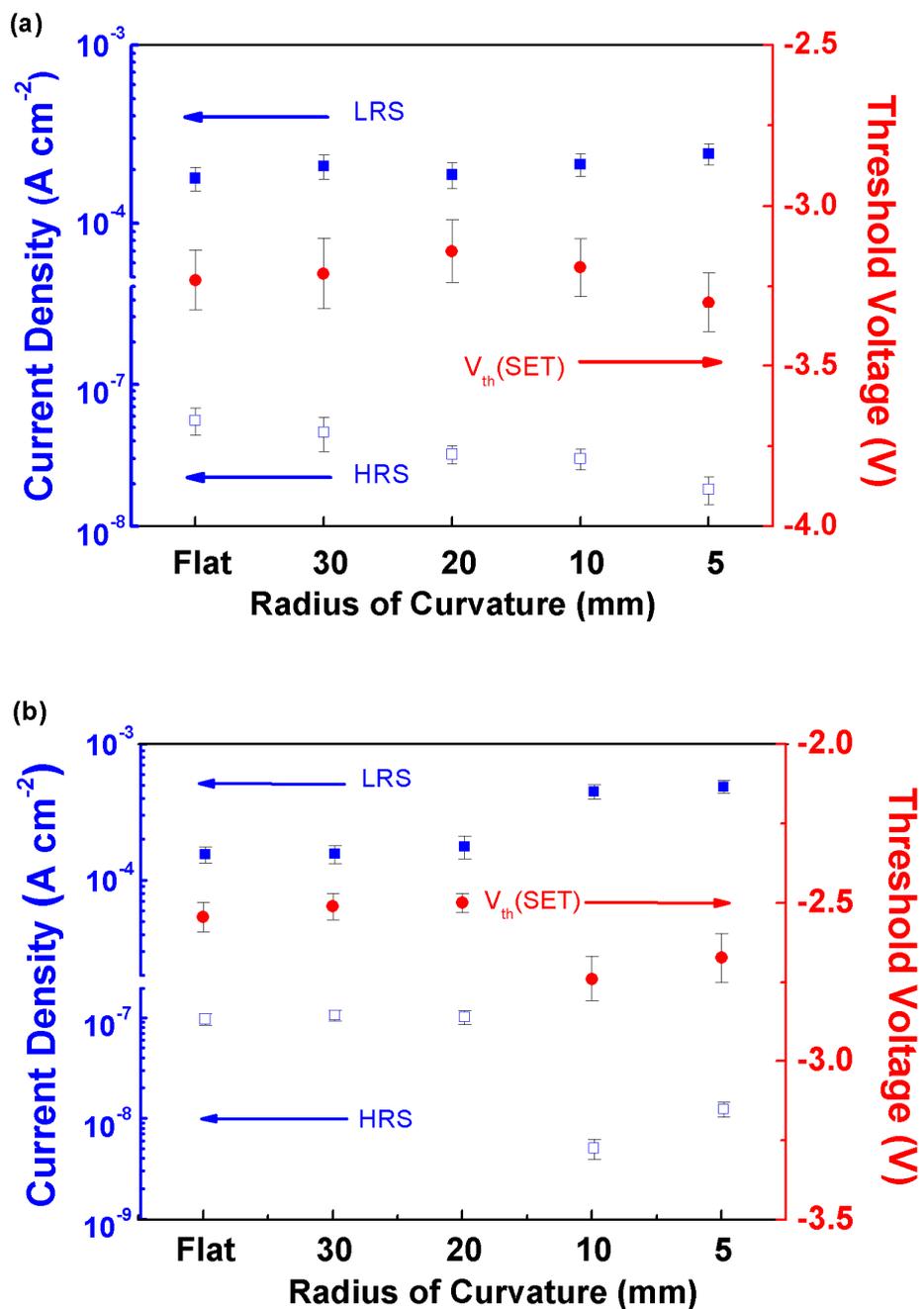


Figure S8. Variation of current density and threshold voltages of flexible WORM memory devices with different bending radii, using the blends of (a) PI(AMTPA):10% and (b) PI(AMTPA):15% PDI-DO.

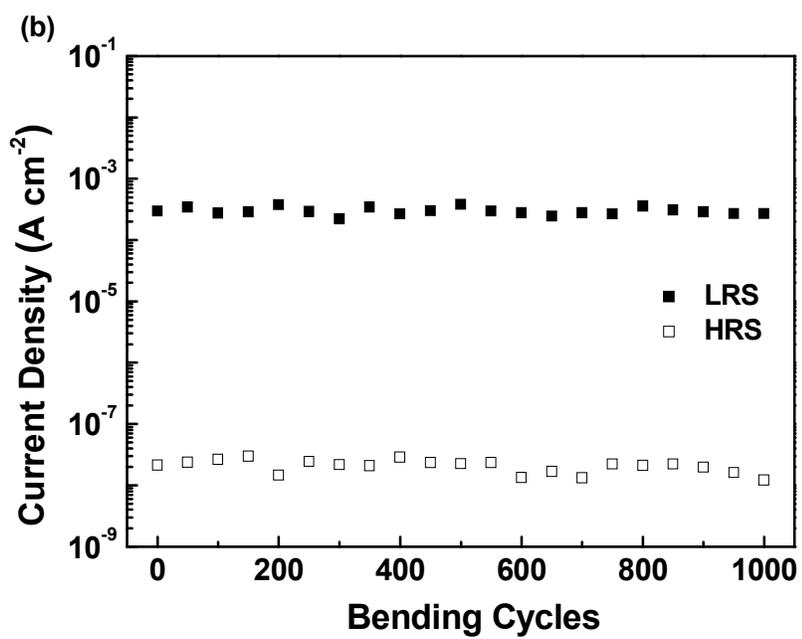
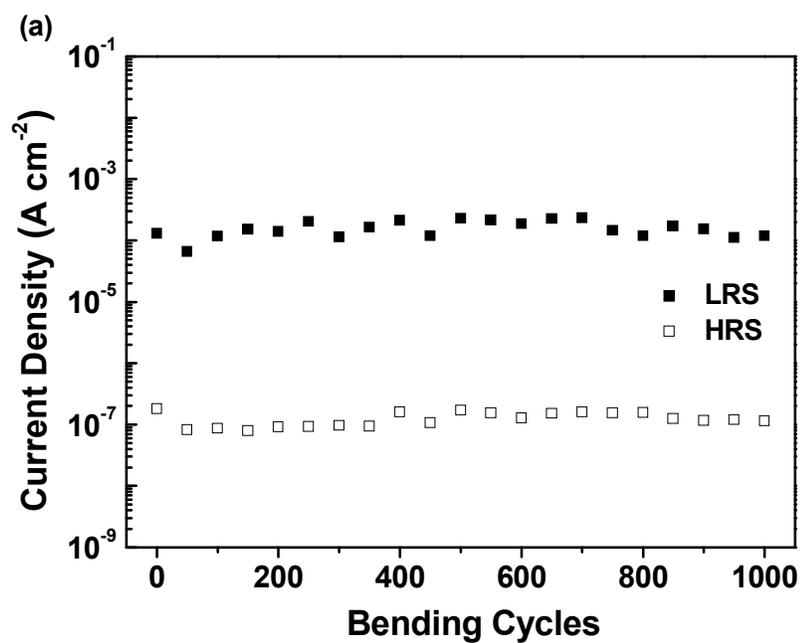


Figure S9. Mechanical endurance of the flexible memory device using the blends of (a)

PI(AMTPA):3% coronene and (b) PI(AMTPA):3% PDI-DO.

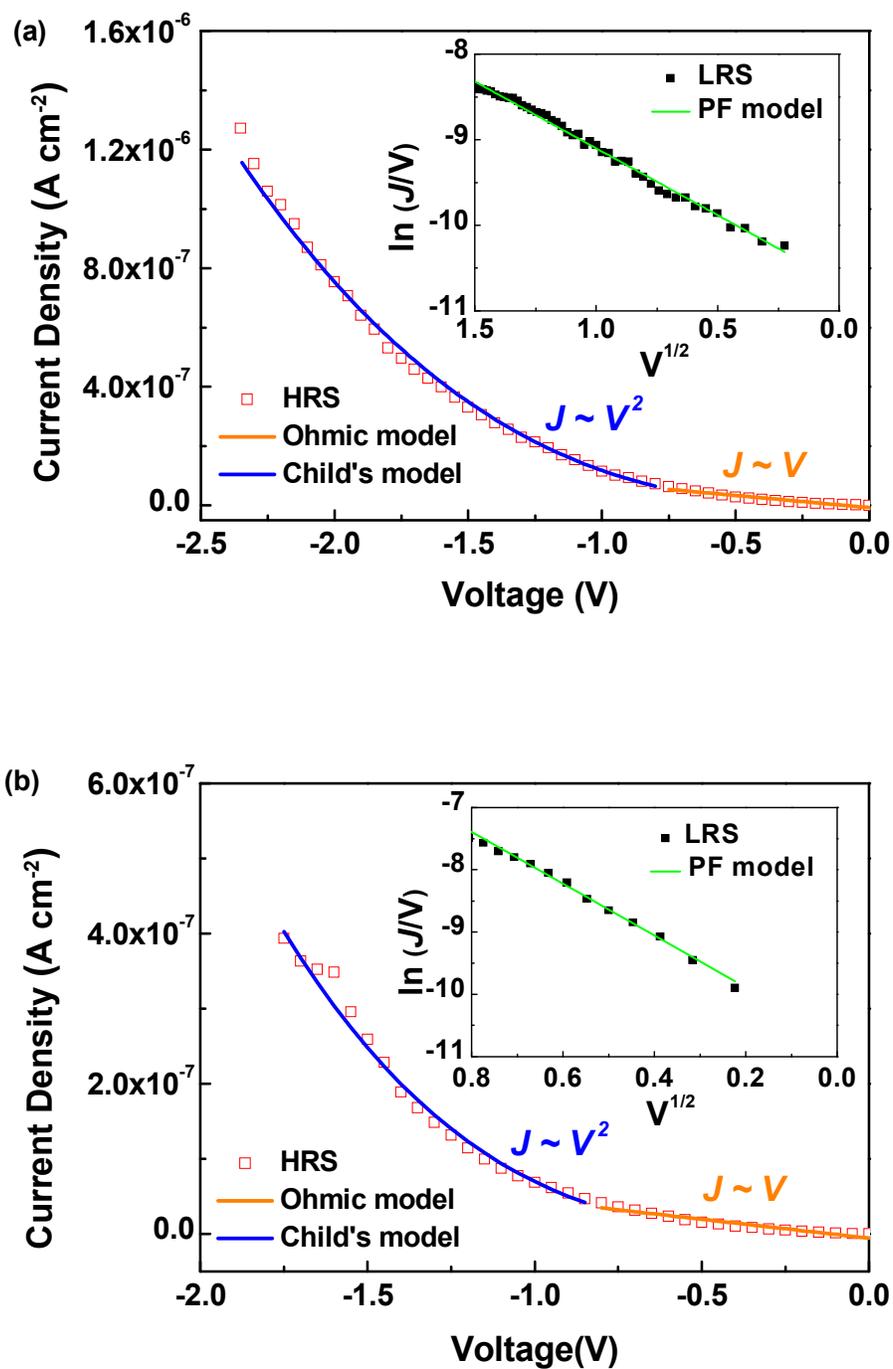


Figure S10. Experimental and fitted J - V characteristics of flexible WORM memory device using the blends of (a) **PI(AMTPA):15%** coronene and (b) **PI(AMTPA):10%** PDI-DO.

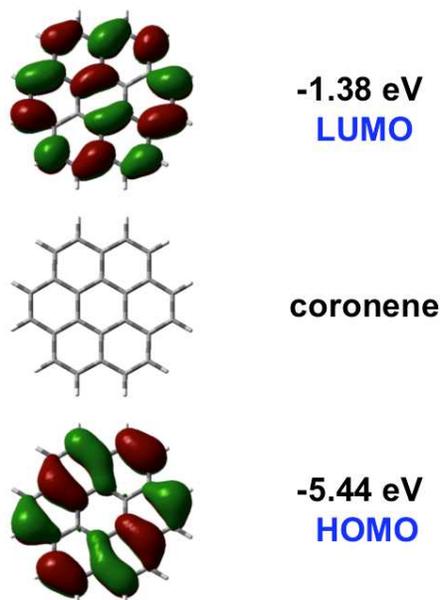


Figure S11. The energy states of coronene.

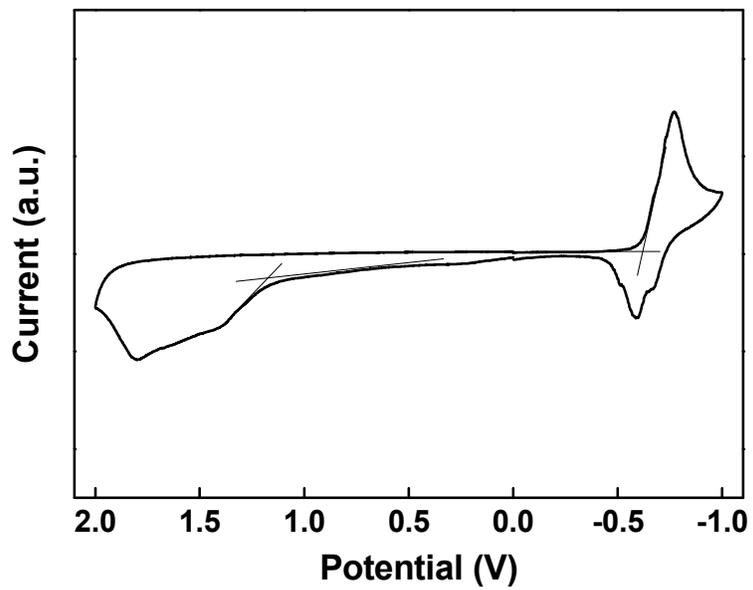


Figure S12. Electrochemical cyclic voltammogram of **PDI-DO**.