

Supplementary Information

Rewritable Resistive Memory Effect in Poly[N-(3-(9H-carbazol-9-yl)propyl)-methacrylamide] Memristor

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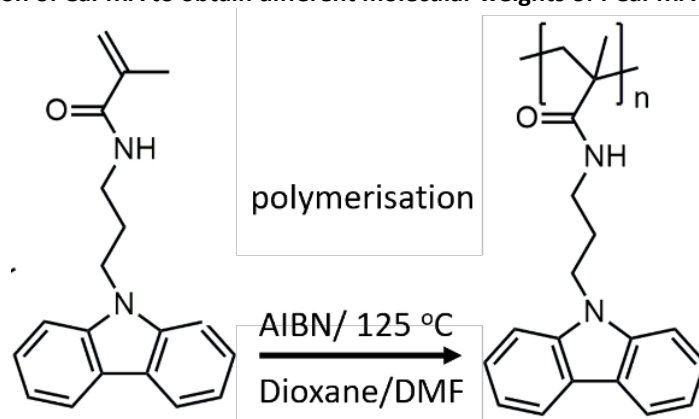
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A) Polymerization of CaPMA to obtain different molecular weights of PCaPMA



The PCaPMA with three different molecular weights were synthesized varying the time and temperature during radical polymerization. The procedure below explains the details of polymerization.

i. **Procedure 1:**

The *N*-(3-(9*H*-carbazol-9-yl)propyl)methacrylamide (1.6114 g, 5.512 mmol) and AIBN (0.0096 g, 1 mol % per monomer) was weighed into a 100 mL three-neck round bottom flask having a reflux condenser, argon inlet, magnetic stirrer, and septum and the system was flushed with argon for 2 h. Then dioxane (16 mL) and toluene (4 mL) were added via septum, and the reaction mixture was heated at 60 °C under argon for 33 h. The precipitation test into methanol was weak. Next, the AIBN (1 mol %) was added, and the reaction mixture was refluxed (145 °C) for 17 h under argon, then cooled down and precipitated into methanol (350 mL). Finally, the yellowish raw polymer was reprecipitated from toluene into diethyl ether (700 mL) to give a nearly white product, filtered off (S4), and dried.

Batch 1 (B#1): Yield = 0.5192 g (32 %); Mw = 2900, Mn = 2100, Đ = 1.38.

¹H NMR (600.27 MHz, DMSO, δ): 8.20-6.80 (m, 9H, carbazole 8H + NH), 4.10 (br s, 2H, carbN-CH₂), 2.87 (br s, 2H, carbN-C-CH₂), 1.77 (br s, 2H, carbN-C-CH₂), 1.60-0.50 (m, 5H, backbone CH₂ + CH₃). ¹³C NMR (150.96 MHz, DMSO, δ): 176.9 (C=O), 139.9, 125.6, 122.2, 120.2, 118.7, 109.1 (6 × 2C carbazole), 54.7, 44.8, 37.5, 27.9, 18.1, 16.6 (6C aliphatic).

ii. Procedure 2

The *N*-(3-(9*H*-carbazol-9-yl)propyl)methacrylamide (1.8533 g, 6.339 mmol) and AIBN (0.0208 g, 2 mol % per monomer) and dried toluene (30 mL) was sealed into an ampoule under argon. First, the polymerization was performed at 100 °C for 124 h, then the content of the ampoule was precipitated into methanol (400 mL), and the raw polymer was reprecipitated from toluene into diethyl ether (700 mL) to give a nearly white product, which was filtered off (S3) and dried.

Batch 2 (B#2): Yield = 0.3905 g (21 %); Mw = 3500, Mn = 2700, Đ = 1.30.

¹H NMR (600.27 MHz, DMSO, δ): 8.20-6.80 (m, 9H, carbazole 8H + NH), 4.08 (br s, 2H, carbN-CH₂), 2.85 (br s, 2H, carbN-C-CH₂), 1.74 (br s, 2H, carbN-C-CH₂), 1.60-0.50 (m, 5H, backbone CH₂ + CH₃).

¹³C NMR (150.96 MHz, DMSO, δ): 176.8 (C=O), 139.7, 125.6, 122.0, 120.2, 118.6, 109.1 (6 × 2C carbazole), 54.4, 44.6, 37.4, 28.0, 17.8, 16.4 (6C aliphatic).

iii. Procedure 3

The *N*-(3-(9*H*-carbazol-9-yl)propyl)methacrylamide (1.810 g, 6.19 mmol), AIBN (0.027 g, 2 mol % per monomer), 1,4-dioxane dried with LiAlH₄ and distilled (13 mL), and DMF anhydrous (3 mL) were sealed in an ampoule under argon and heated at 65 °C (28 h), 70 °C (44 h), 100 °C (24 h), and 125 °C (147 h). Then the content of ampoule was precipitated into diethyl ether (900 mL), the raw white polymer was filtered off (S3) and reprecipitated from dioxane/DMF (15/5 mL) into diethyl ether (900 mL). The white polymer was left for sedimentation, then filtered off (S3) and dried (oil pump).

Batch 3 (B#3): Yield = 1.4133 g (78 %); Mw = 6000, Mn = 4000, Đ = 1.50.

¹H NMR (600.27 MHz, DMSO, δ): 8.20-6.80 (m, 9H, carbazole 8H + NH), 4.06 (br s, 2H, carbN-CH₂), 2.86 (br s, 2H, carbN-C-CH₂), 1.73 (br s, 2H, carbN-C-CH₂), 1.60-0.50 (m, 5H, backbone CH₂ + CH₃). ¹³C NMR (150.96 MHz, DMSO, δ): 176.8 (C=O), 139.7, 125.6, 122.0, 120.2, 118.6, 109.0 (6 × 2C carbazole), 54.8, 44.6, 37.4, 27.8, 17.8, 16.2 (6C aliphatic).

B) Etching of ITO coated on a glass substrate (fabrication of BE)

ITO coated glass substrates (un-patterned) (thickness 100 nm) were purchased from Ossila (Netherland) and then patterned using zinc powder (Sigma Aldrich, USA), and hydrochloric acid (Lach:ner, Czech Republic) to form a bottom electrode of 2 mm wide. At first, the specified part was covered with adhesive tape followed by the sputtering of zinc powder and dropping of hydrochloric acid. The sample was then immediately dipped into the distilled water. The longer the dropping, the more corrosion of ITO takes place, so the time should be shortened as possible.

C) Schematic of fabricated device

ReRAM devices with polymer layer sandwiched between ITO as a bottom electrode (BE) and Al or Au as top electrode (TE) is prepared as in Fig. S1. The active areas between the electrodes were 0.15 and 2 mm² formed after cross section of TE and BE with polymer layer in between. As TE, 5 electrodes were cast by physical vapor deposition (PVD) using the shadow mask.

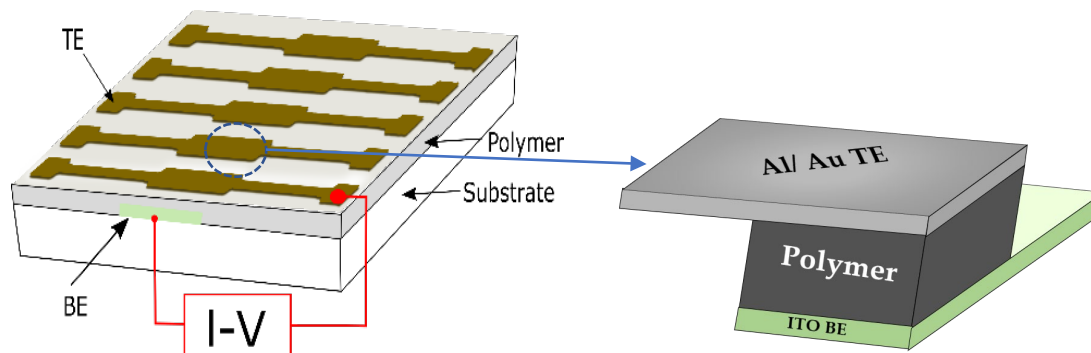
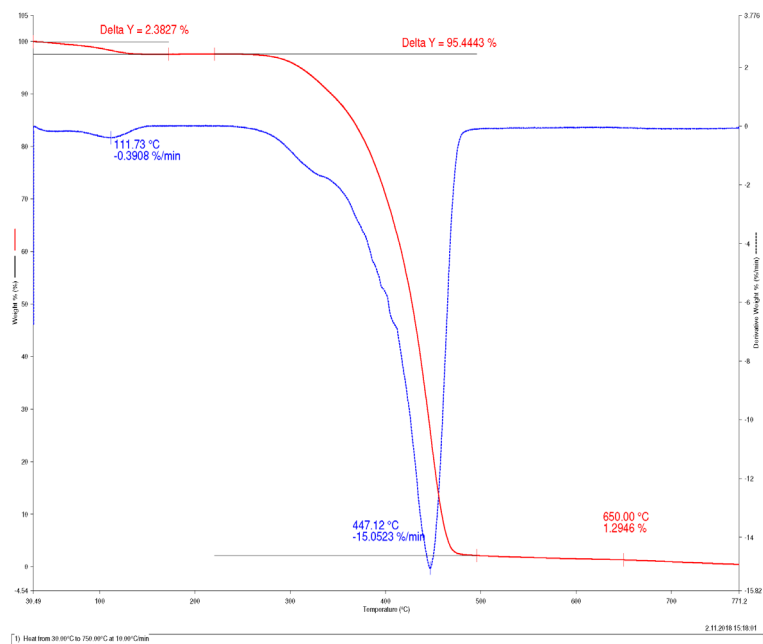


Fig. S1: Schematics of a memory device. "TE" and "BE" indicates Top electrode (Au or Al) and bottom electrode (ITO).

D) Thermal analysis

a



b

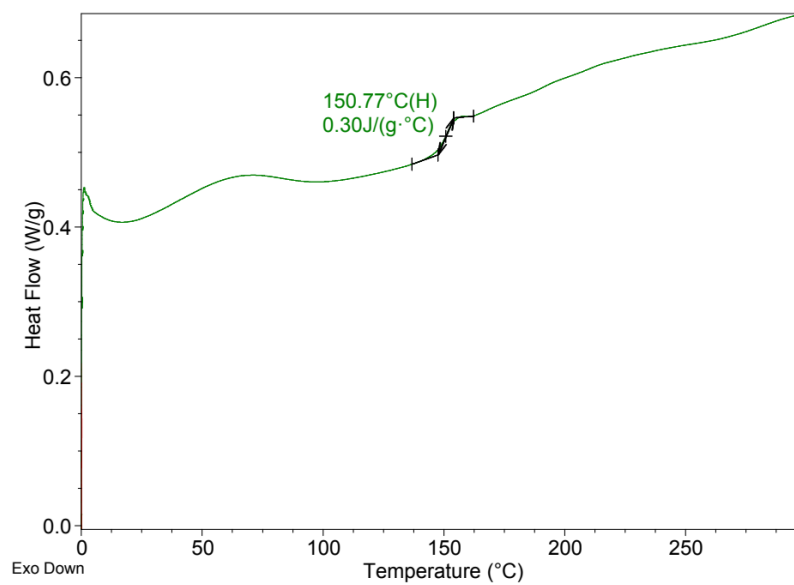


Fig. S2: TGA (a) and DSC (b) curves of the polymer PCaPMA. Heating was 10 °C/min for TGA and 5 °C/min for DSC.

E) UV-vis and PL spectra of three batches of PCaPMA differing in molecular weight (and PVCa as a reference polymer).

All polymers synthesized with different molecular weights prepared within this study showed complete spectral overlap in UV-vis and fluorescence spectra as shown in Fig. S3. PCaPMA with Mw: 6000 was further used for this study.

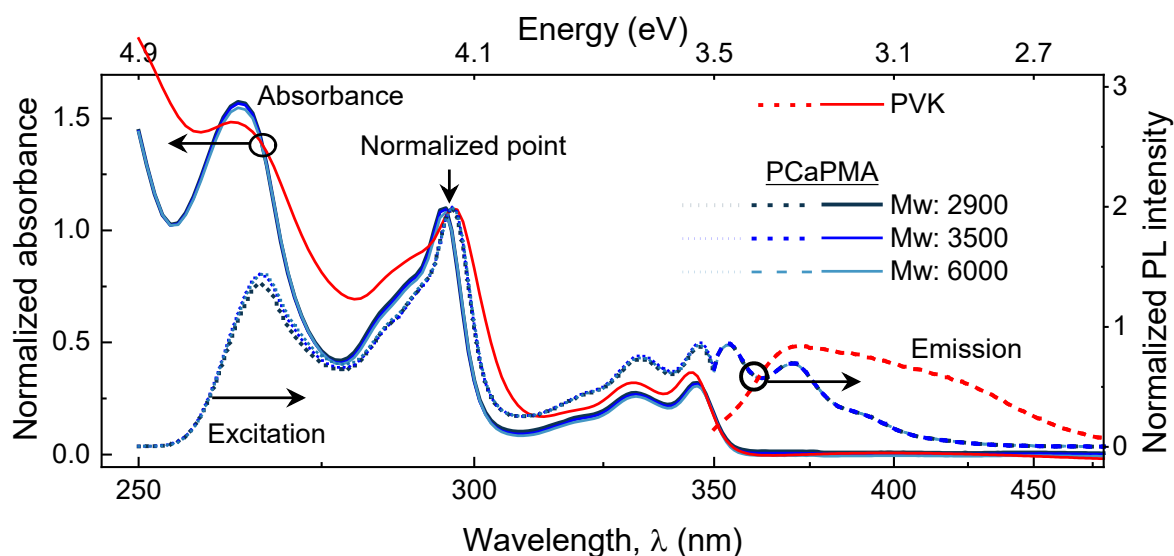


Fig. S3: Excitation (dotted lines), emission (dashed lines), and UV-vis absorption (solid lines) spectra of DMSO solutions of three batches of PCaPMA (cyan, light blue and dark blue lines), prepared using different reaction times and temperatures during radical polymerization. For comparison, absorption and emission spectra of PVCa are shown in red color. (In all cases: excitation wavelength: 344 nm, emission wavelength: 373 nm were used and solution concentration was 10^{-5} M in DMSO).

F) Profilometry

We employed a Tencor P-17 stylus profilometer (KLA, U.S.A.) to make a 3D scan of the surface of the film. Using this technique seemed to be adequate with regards to the sample dimensions and to the film thickness in particular. The scan was performed on different selected areas with the scan speed of 2 mm/s (minimum available speed), 2000 Hz bandwidth for acquiring highest possible amount of data, and the scanning density 1 line per 500 nm. No pinholes were observed in the scan of multiple regions of the layer with thickness about 100 nm. Fig. S4a shows the 3D scan of the area $20 \times 20 \mu\text{m}$ with high resolution. The average roughness was found to be in the range of 2-5 nm from this measurement. No visible hole that extends deeper than 10 nm has been detected. Fig. S4b shows the scan of another area with the scratch made intentionally and reaching the surface of substrate. It proves that the film is very homogeneous compared to the thickness. Fig. S4c shows one scan across the scratch from which the thickness can be determined.

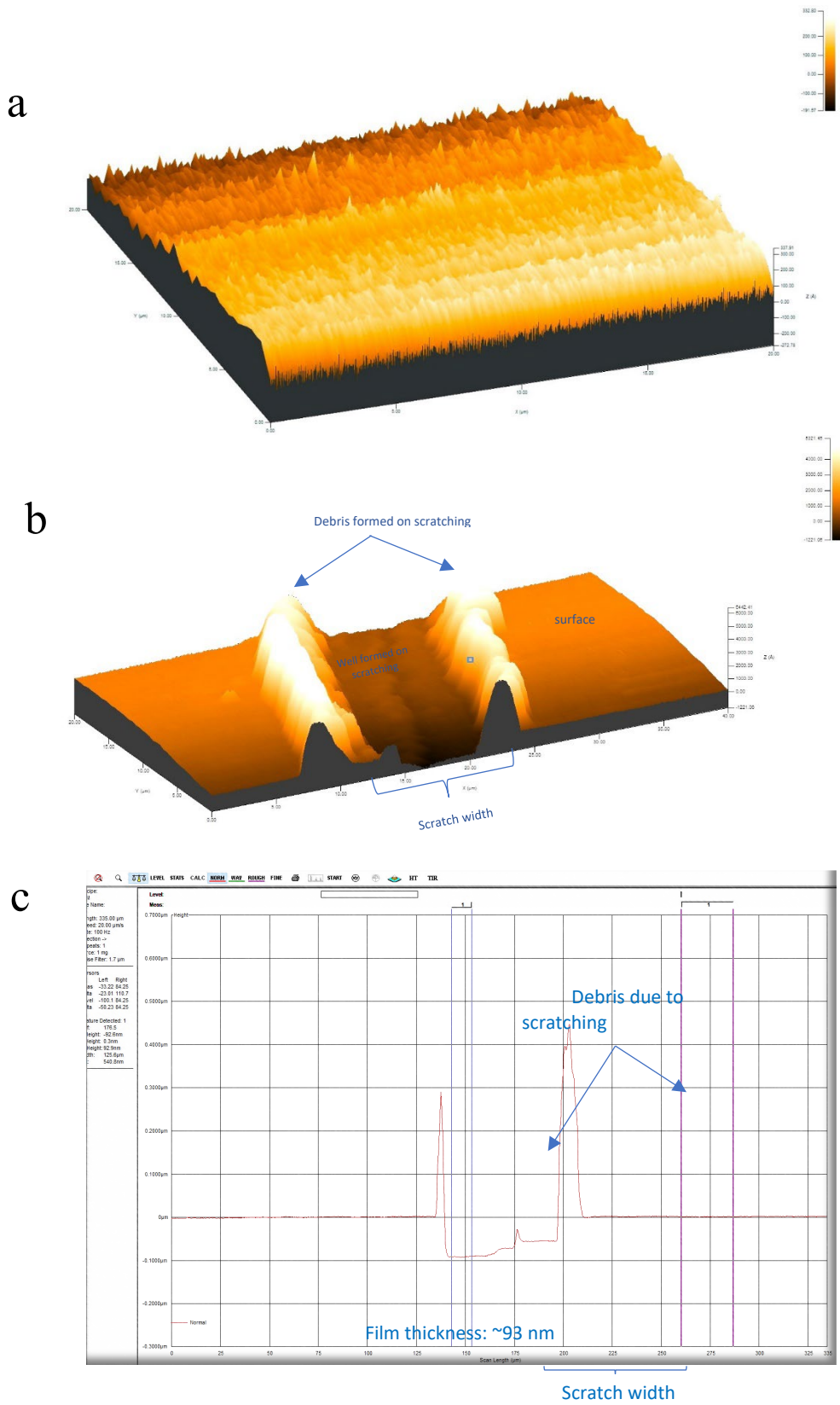


Fig. S4: a) 3D scan of the film surface roughness using surface profiler, b) 3D-scan for probing thickness, c) a single scan across the scratch from which the thickness can be determined

G) Temperature dependence of the spectra of the dielectric constant

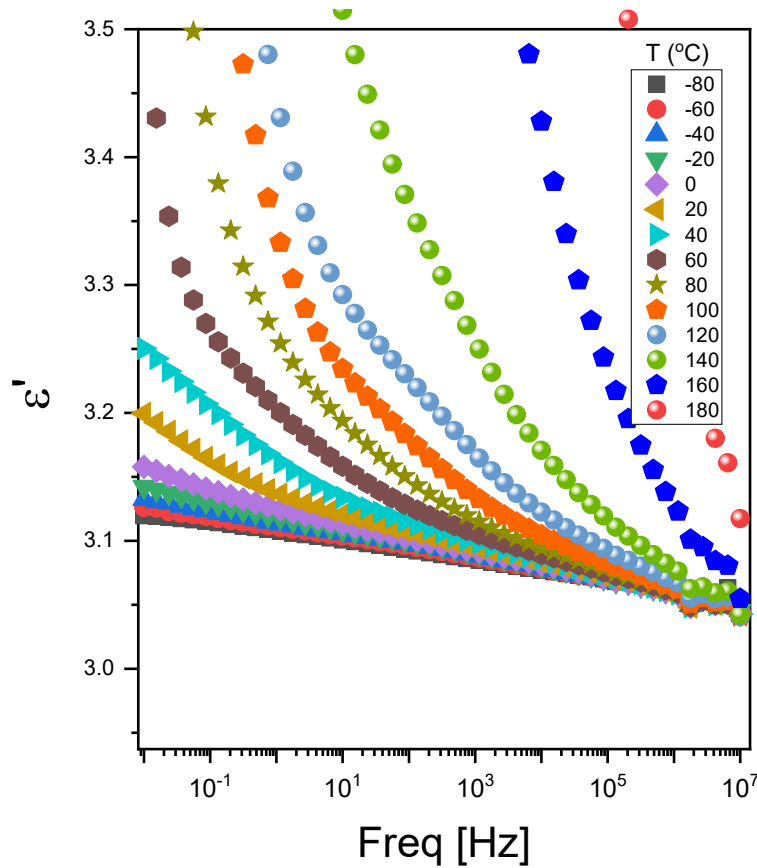


Fig. S5: Temperature dependence of the spectra of the dielectric constant.

H) Volatility test

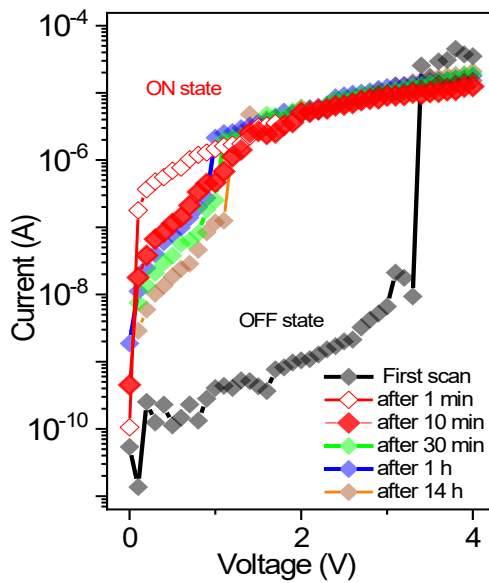


Fig. S6: Volatility test of memory device over different periods of time with voltage sweep in ambient environment.

Fig. S6 illustrates persistence of the device in the ON state after switching. The experiment involved repeated voltage sweeps from 0 to +4 V with varying time delays between each sweep, and the device's conductivity was measured at room temperature in air. Repeated voltage sweeps from 0 to +4 V was applied with varying time delay in between and the conductivity of the device was measured. After the first sweep that switched the device to the ON state at around +3.5 V, the sample was allowed to relax without any applied voltage for 1 minute. During the subsequent sweep, the conductivity was found to be almost unchanged. After a relaxation period of 10 minutes, the following sweep exhibited the current values decreased by nearly an order of magnitude, but the ON state was recovered at about 1 V. Notably, this voltage is remarkably smaller compared to the first sweep. As the time interval between subsequent sweeps increased, a slight decrease in current was observed; however, the device didn't fully relax back to the OFF state, demonstrating the non-volatile behavior of the device. These findings indicate the device's ability to maintain its conducting state over extended periods, making it a promising candidate for nonvolatile resistive memory applications.

I) Current density

Two ITO/PCaPMA/Al structures with two different active areas, one measuring 0.15 mm^2 and the other 2 mm^2 , were prepared and subjected to characterization. Both devices exhibited almost identical current density values.

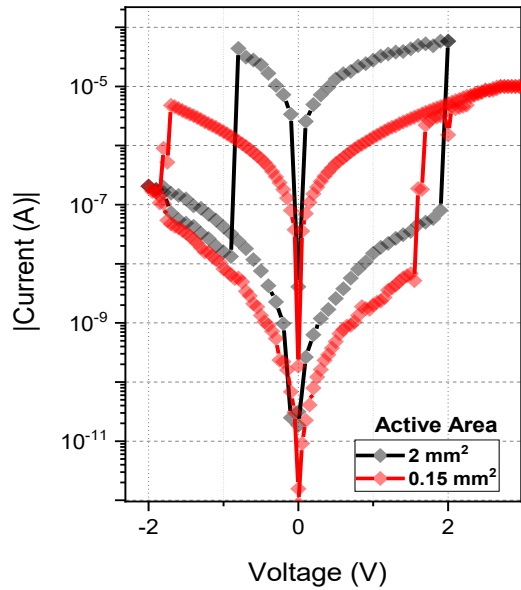


Fig. S7: I-V characteristics of ITO/PCaPMA/Al samples with two different active areas 2.0 and 0.15 mm^2 , respectively.

J) Current evolution with temperature

The temperature-dependence of conductivity of the ITO/PCaPMA/Al device was investigated in both the ON and OFF states in quasi-static regime. First, the temperature dependence of the current was measured in the OFF, starting from $20 \text{ }^\circ\text{C}$ up to $100 \text{ }^\circ\text{C}$ with $15 \text{ }^\circ\text{C}$ step. Subsequently, smaller $5 \text{ }^\circ\text{C}$ steps were used between $100 \text{ }^\circ\text{C}$ to $130 \text{ }^\circ\text{C}$. The current was recorded after allowing 15 min for temperature stabilization at each step. Once the device was cooled back to $20 \text{ }^\circ\text{C}$, the same measurement procedure was repeated for the device switched to the ON state following the same temperature steps as in the OFF state.

In the ON state, the current displayed barely observable dependence on temperature. However, in the OFF state, the current was thermally activated. The temperature-dependent behavior was well-described using an Arrhenius plot, yielding the activation energy $E_a = 0.33 \text{ eV}$.

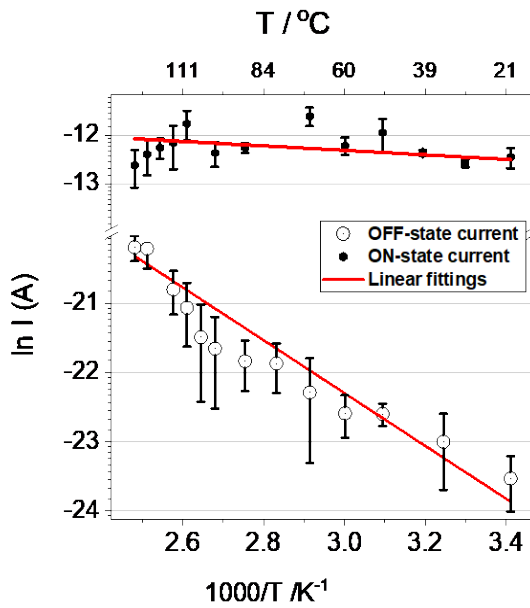


Fig. S8: Arrhenius plots of the ON state (solid dots) and OFF state (empty dots) currents, measured using 1 V and 5 V , respectively. The measurements were performed on the same device with a PCaPMA layer thickness of 90 nm and inside vacuum. The linear fitting (red line) illustrates the Arrhenius plot.

K) Optical detrapping.

The presence of trapped charges was proved by the photodetrapping experiment on device I in a vacuum, pressure of 5×10^{-4} mbar. With electric field applied in dark, charge carriers were injected and trapped in localized states. Upon optical illumination, a decay current was observed caused by charges released from traps. In the unbiased sample (without a previously applied electric field), no current decay was observed upon the same optical illumination. This observation proves the presence of charges trapped in localized levels.

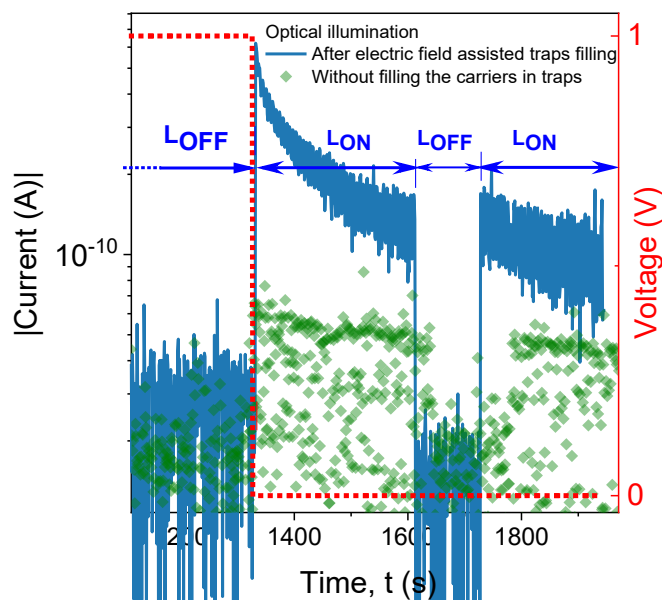


Fig. S9: Photodetrapping of trapped charges in device I after previous bias at +1 V (blue curve). Photocurrent measured at the same conditions but without previously applied voltage is shown for comparison (green dots). Applied voltage shown as red dotted line. Sample thickness 80 nm, electrode area 2 mm², illumination through the glass/ITO side using Xe-lamp equipped with a bandpass filter, light intensity 400 $\mu\text{W}/\text{cm}^2$. L_{ON} and L_{OFF} show the time periods with and without illumination, respectively.

L) Film parameters at various preparation conditions

Table S1: Film parameters at various preparation conditions.

Solvent	Solution conc. (mg/ml)	Filter pore size (nm)	Revolving speed (rpm)	Thickness (nm)
	11	100	2000	35
	11	100	3000	30
	33	100	2000	95
	33	100	3000	80
Chlorobenzene (b.p. 132 °C)	55	220	2000	170
	55	220	3000	155
	110	400	2000	505
	33	100	2000	210
	33	100	3000	240
Chloroform (b.p. 61 °C)	55	220	2000	450
	55	220	3000	505