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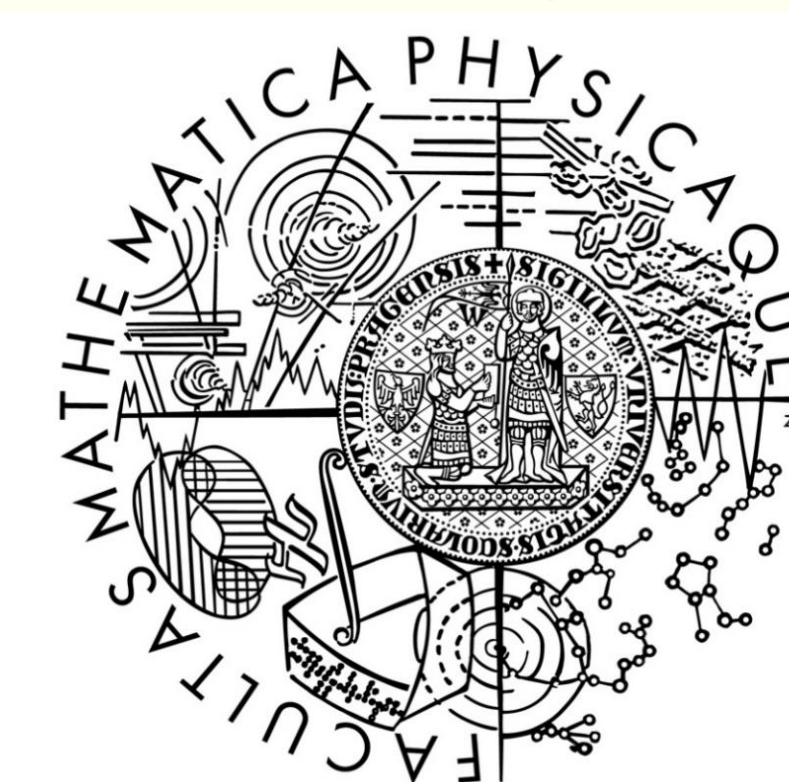
# Rewritable Electrical Memory Effect in Poly[N-(3-(9H-carbazole-9-yl)propyl)methacrylamide](PCaPMA)

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A memristor is principally a resistor-like device composed of an active layer sandwiched between two electrodes whose resistance is dependent on the magnitude and direction of the previously applied voltage, and exhibits at least two distinct electrical conductance states. These states can be assigned to binary state of logic 0 and logic 1. The devices can be used in switching, high-density information storage, neuromorphic computing and synaptic learning.

Here, we report on synthesis of poly[N-(3-(9H-carbazole-9-yl)propyl)methacrylamide] (PCaPMA), and its photophysical and electrical properties. Thin films of the PCaPMA sandwiched between two metal electrodes exhibit bi-stable resistance with an ON/OFF ratio exceeding 100, good reproducibility and persistence ability. Memristive behaviour has been assigned to charge trapping and stabilization of voltage-induced conformational changes by physical crosslinking via hydrogen bonds between amide and carbonyl groups.

## Synthesis of PCaPMA

### a. Monomer synthesis

N-(3-(9H-carbazol-9-yl)propyl)methacrylamide (CaPMA):

#### i. Carbazole

- (+ acrylonitrile+ benzyltrimethyl- ammonium hydroxide)
- Cooled to 0-5 °C → Rxn temperature increased to 70 °C
- Yellow crystals were filtered off after cooling, and the mother liquor was reduced to get a second crop of crystals.

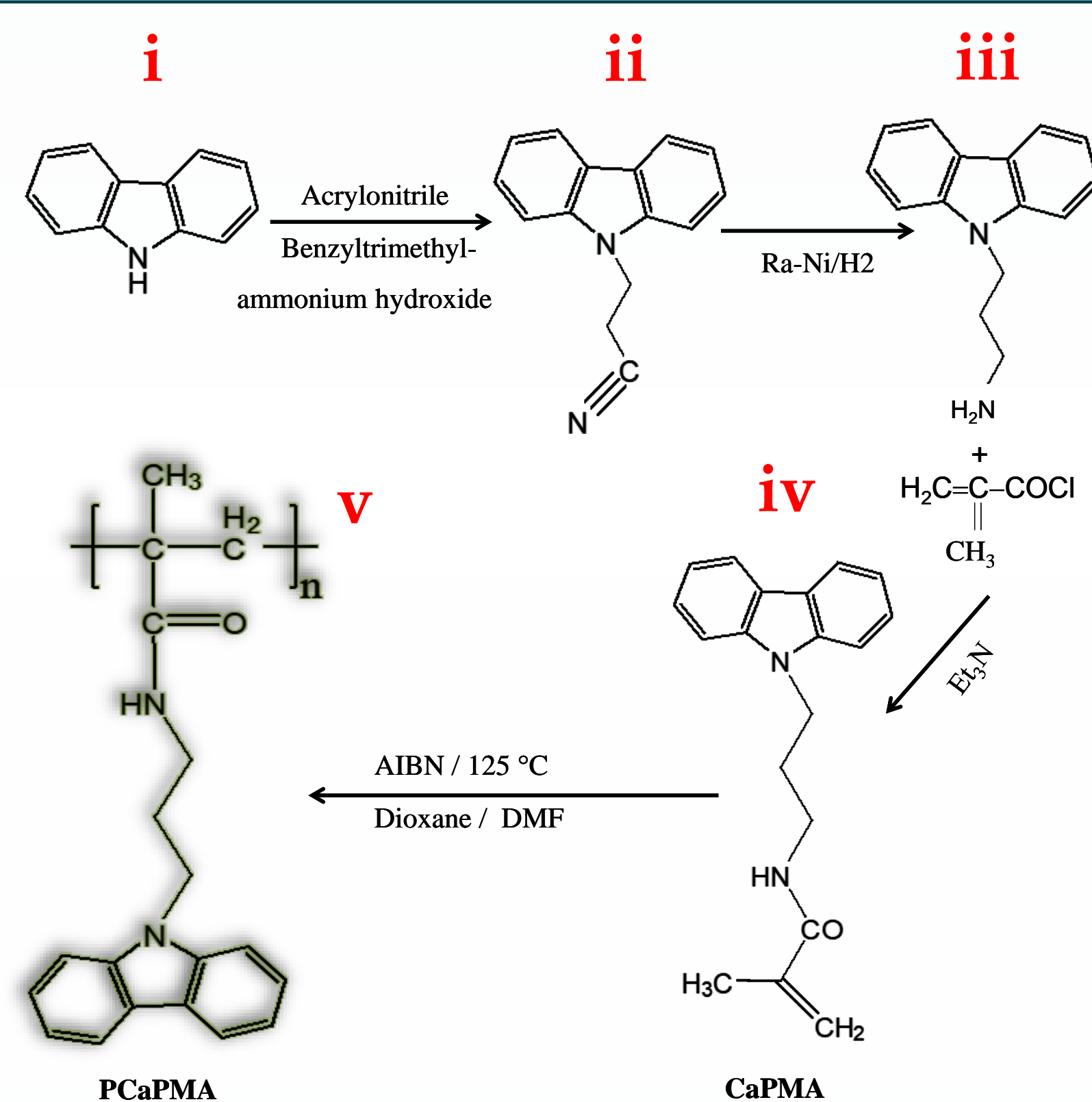
#### ii. 3-(9H-Carbazol-9-yl)propanenitrile (+dioxane+Raney Nickel)

- Catalytic reduction by hydrogen.
- The Raney nickel was filtered off, and dioxane was removed by a rotavapor.
- The amine was vacuum distilled to give a viscous fluorescent liquid that solidifies.

#### iii. 3-(9H-Carbazol-9-yl)propan-1-amine (+ methacryloyl chloride + trimethylamine)

- Increased white suspension was stirred and filtered off.
- The white suspension was washed with water to remove trimethylamine hydrochloride.
- Raw material was crystallized from ethanol (charcoal) to give a white crystal of the title compound.

#### iv. N-(3-(9H-carbazol-9-yl)propyl)methacrylamide

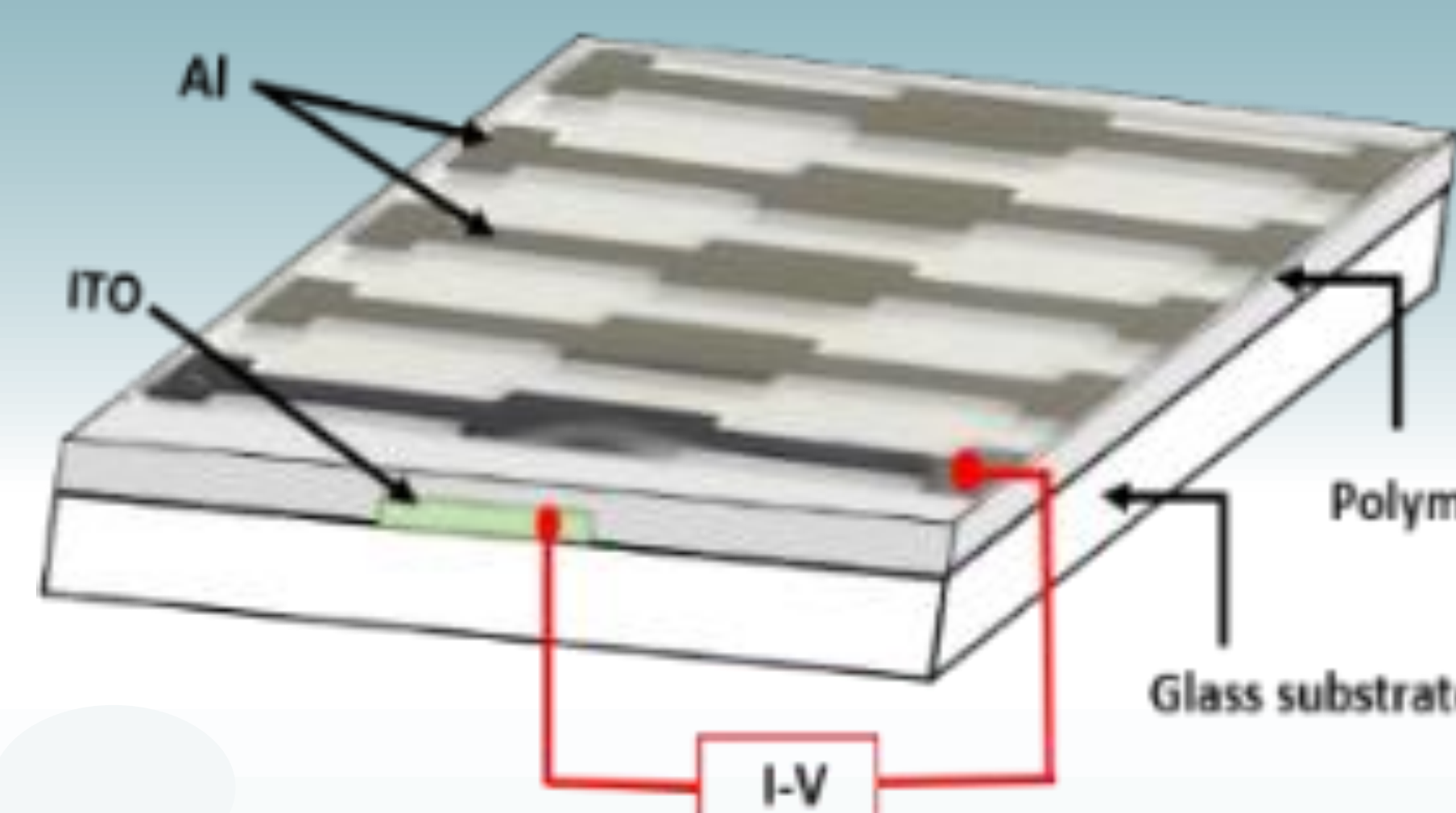


### b. Polymerization

N-(3-(9H-carbazol-9-yl)propyl)methacryl amide  
(+ AIBN+dioxane +DMF)

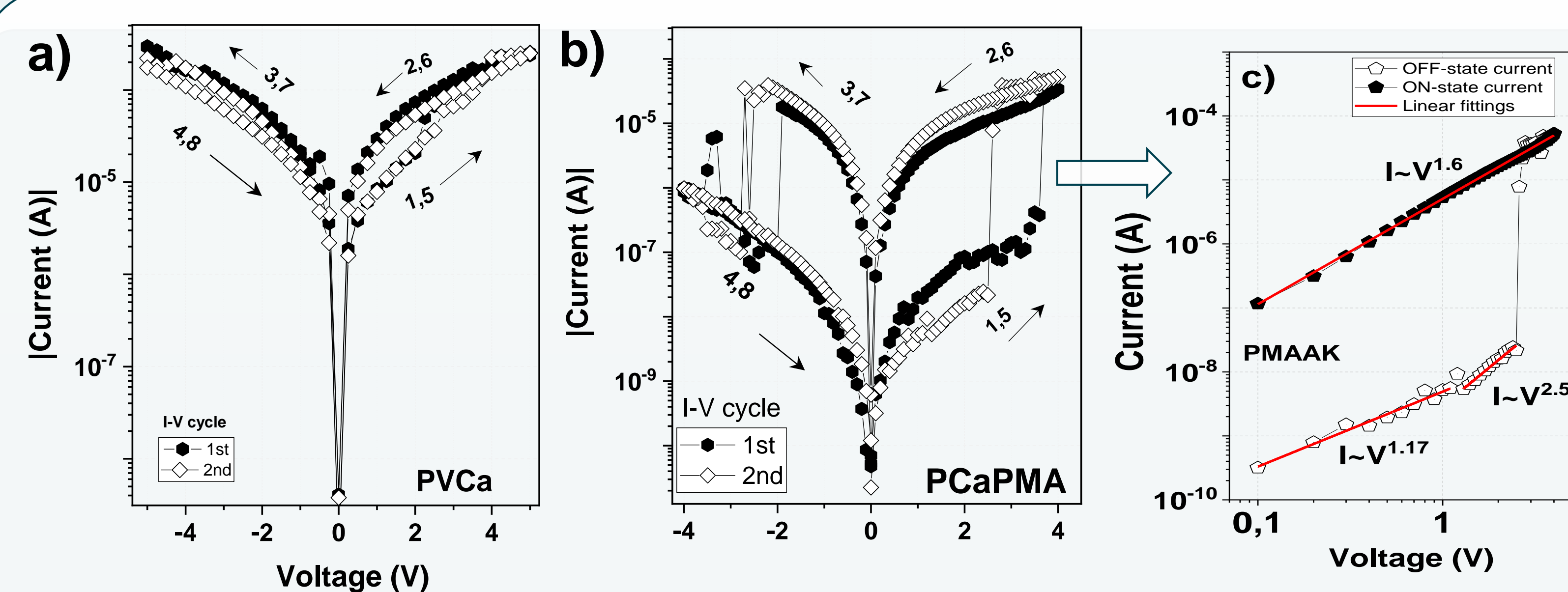
- Mixed compounds were sealed in an ampoule under argon and heated.
- Content of ampoule was precipitated into diethyl ether
- Raw white polymer was filtered off and reprecipitated.
- The white polymer was left for sedimentation, then filtered off and dried.

#### v. PCaPMA



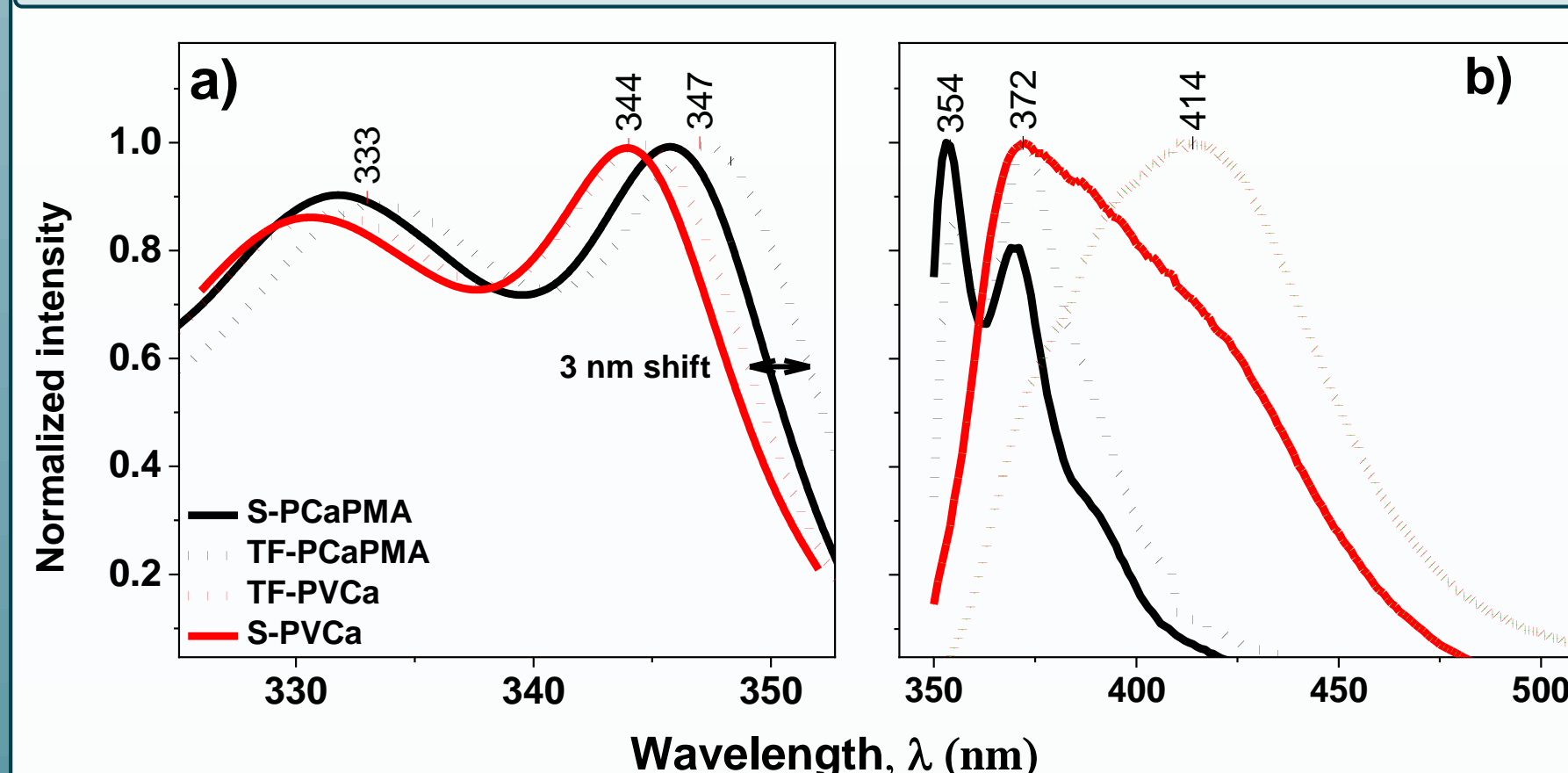
Schematic structure of the memory device: Al as the top electrodes and ITO as the bottom electrode perpendicular to Al.

## Electrical characterization (Memory effect)

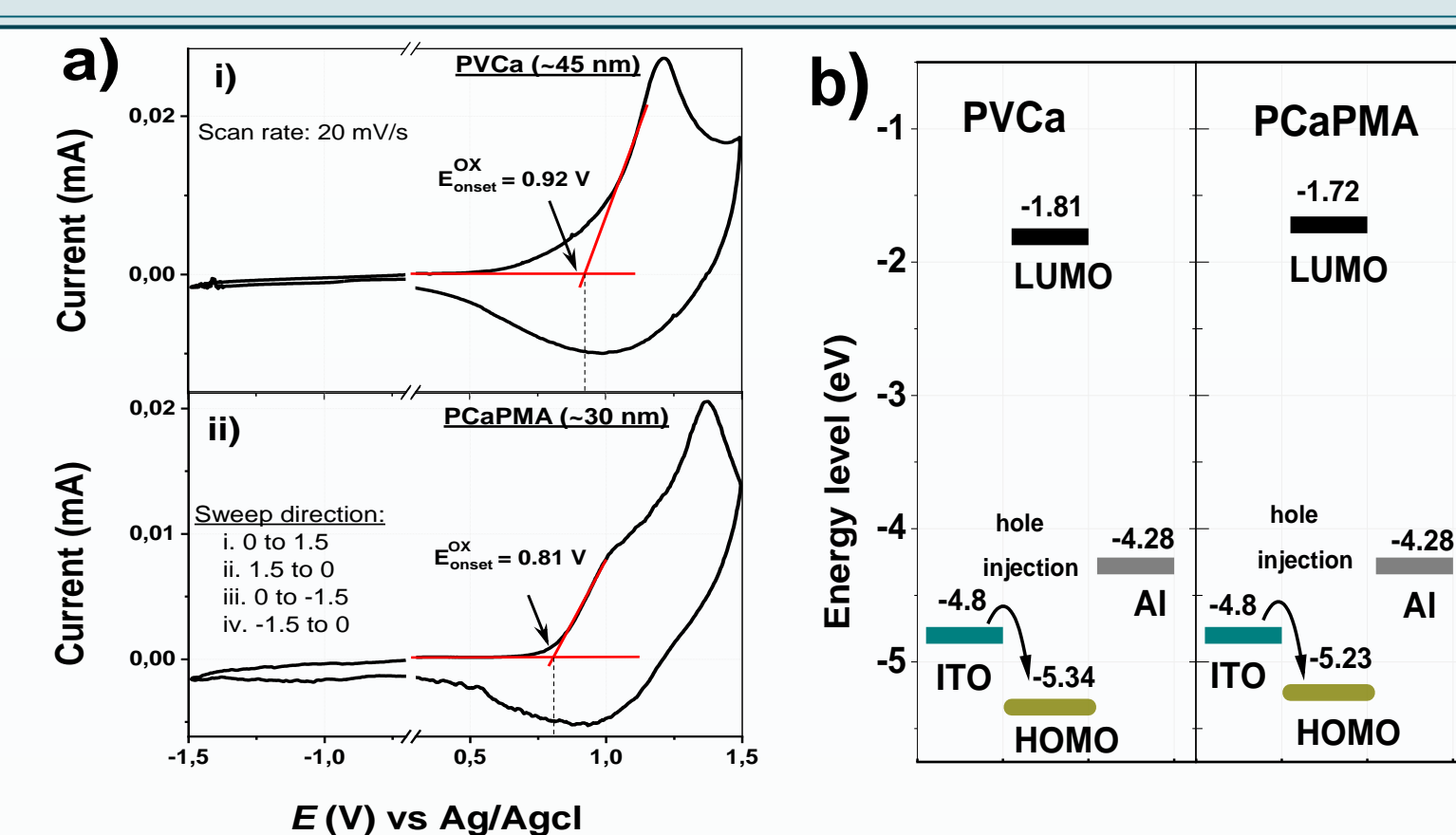


I-V cycles of a) ITO/PVCA/Al and b) ITO/PCaPMA/Al devices in two continuous cycles, sweep order indicated by respective arrows. c) linear fittings of first I-V cycle of PCaPMA in log-log scale for the illustration of transport properties.

## Photophysical and dielectric study

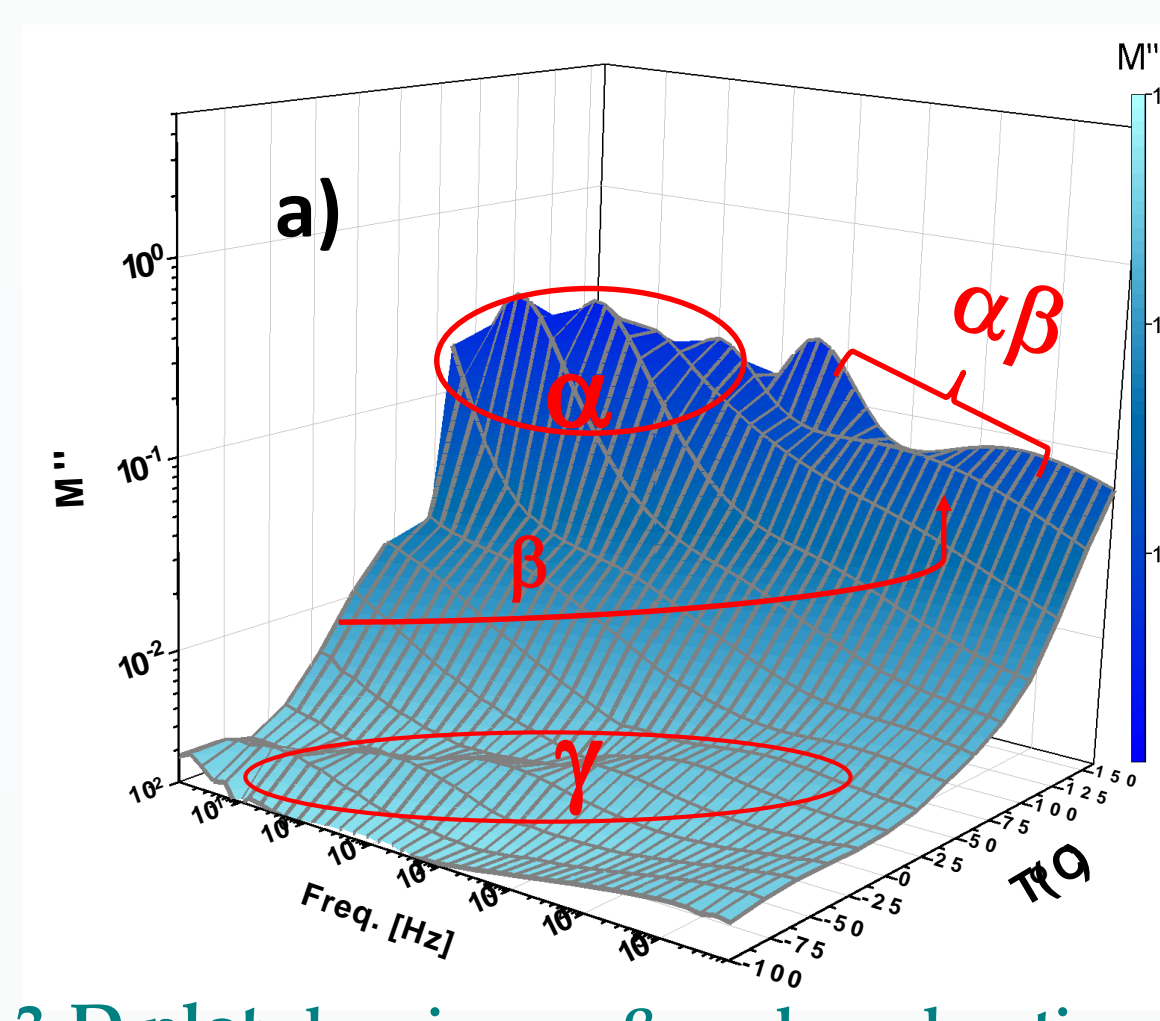


a) UV-Vis and b) emission spectra of both thin films and solutions of PVCA and PCaPMA.

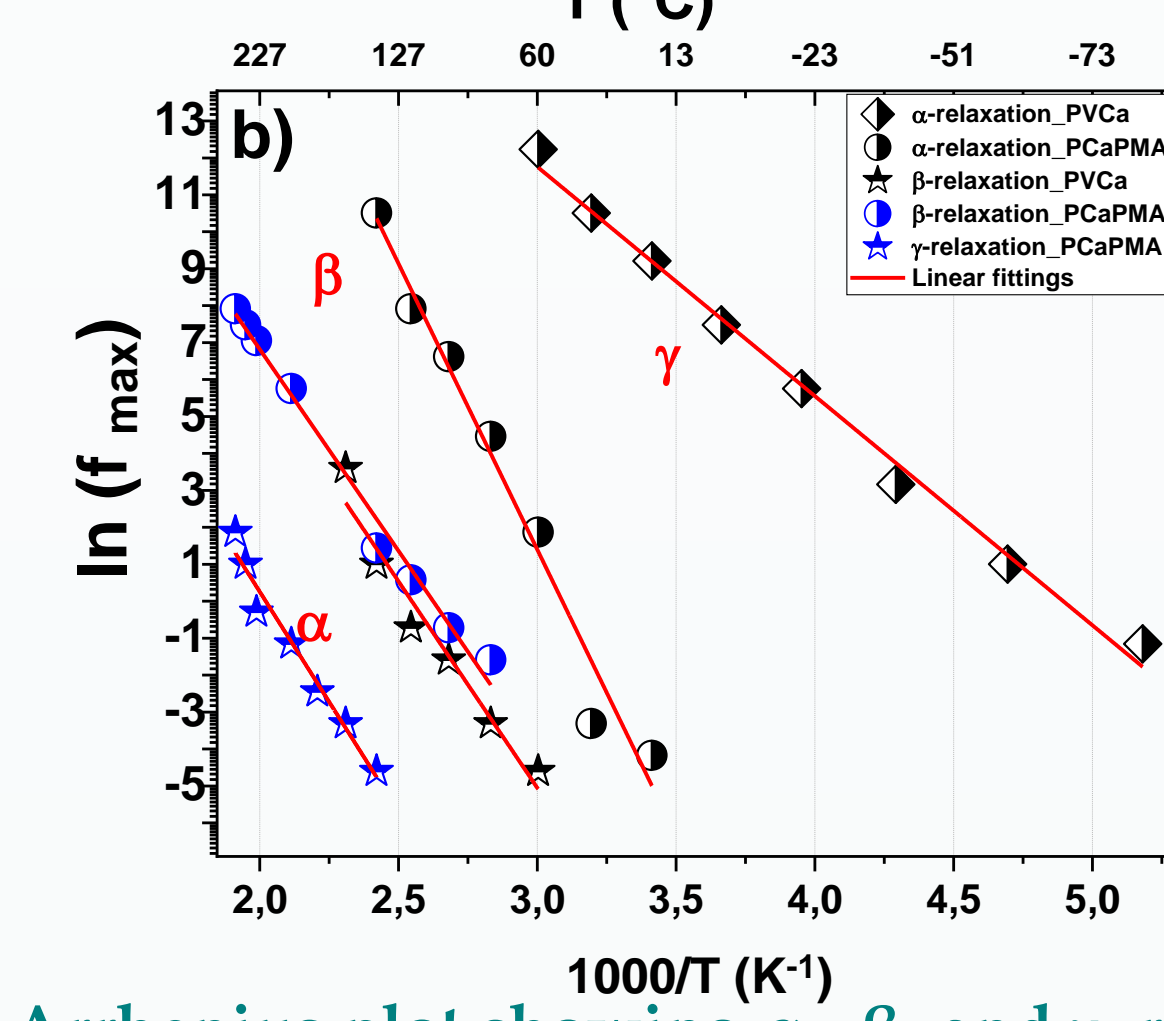


Cyclic Voltammetry measured on polymer thin film (~30 nm) coated on ITO and measured in 0.1 M acetonitrile solution of n-Bu4NPF6. PVCA: Bandgaps (E<sub>g</sub>): 3.53 eV; HOMO: -5.34 eV; LUMO: -1.81 eV. PCaPMA: E<sub>g</sub>: 3.51 eV; HOMO: -5.23 eV; LUMO: -1.72 eV

## Temperature–frequency dependence of the loss modulus (M'')



a) 3-D plot showing α-, β- and γ-relaxation



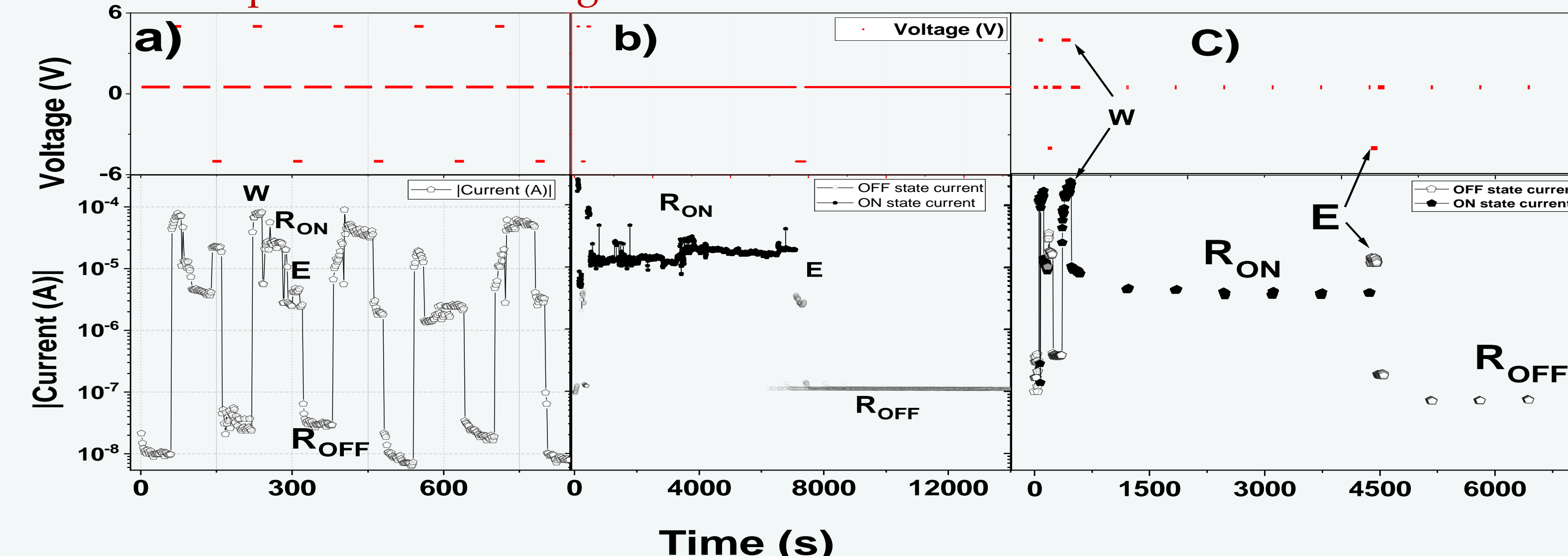
b) Arrhenius plot showing α-, β- and γ-relaxation

## Results

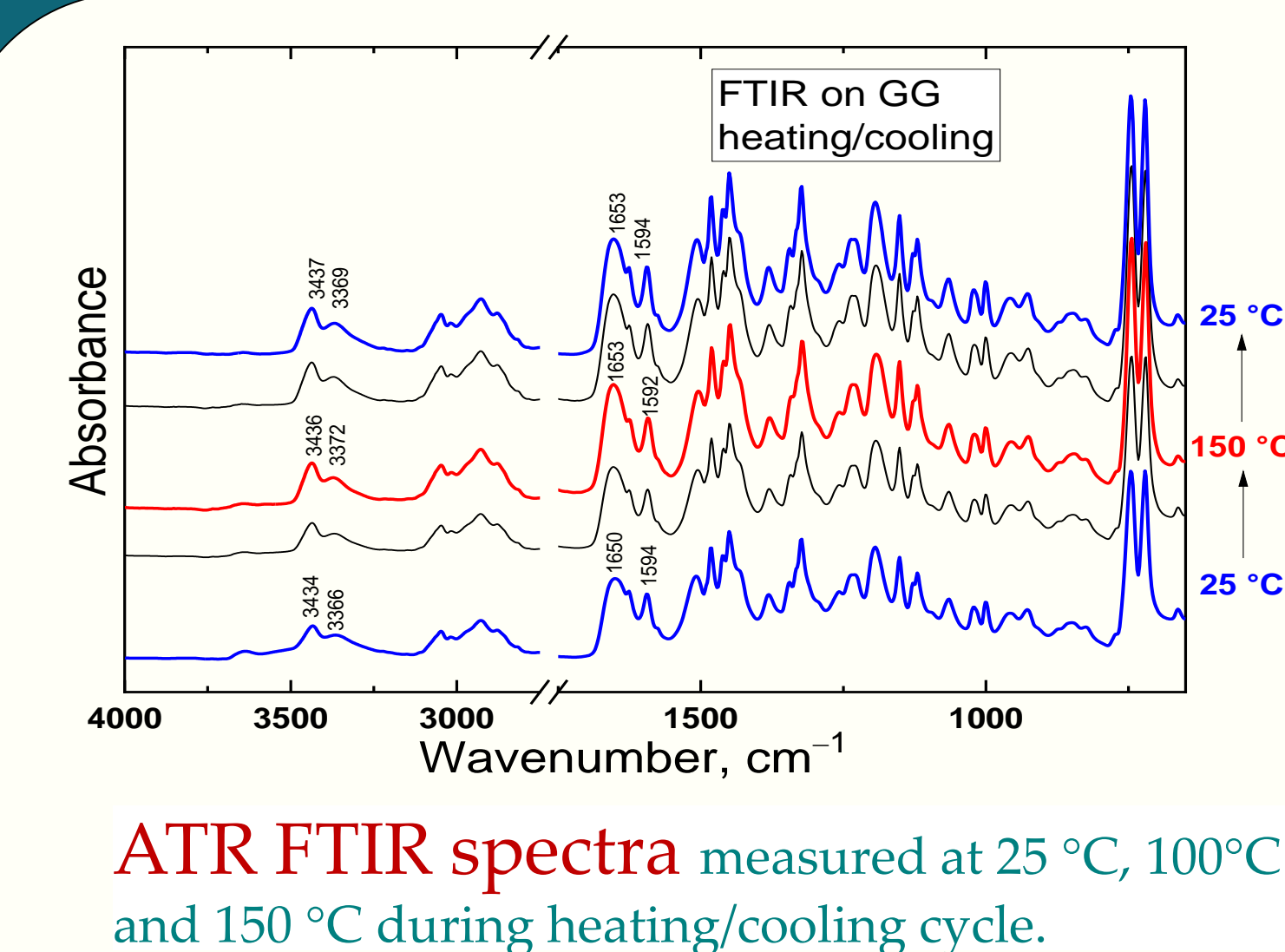
- PCaPMA exhibited good solubility in many organic solvents, high glass transition temperatures ( $T_g = 160$  °C) and high stability at ambient environment.
- The UV-Vis absorption spectra showed sandwich-type aggregations of carbazoles with their highly possible overlapping by the formation of intra- or intrachain excimer.
- Electrochemical study showed the similar energy levels and bandgap as of commercial poly(N-Vinyl carbazole) (PVCA) and proved the hole-transporting property of polymer.
- Broadband dielectric spectroscopic study showed three relaxations properties viz. γ- β- and α- relaxation and proved the thermally-activated conduction behavior of polymer.
- DC current-voltage (I-V) characteristics of sandwiched device showed the abrupt switching and erasing maintaining high ON/OFF current ratio and making device rewritable for memory. The device showed non-volatile behavior.
- Temperature-dependent attenuated total reflectance (ATR) Fourier-transform infrared (FTIR) spectra proved formation of polymer network by physical crosslinking via H-bonds supported by HN-C=O group.
- For the confirmation and calculation of number of traps in thin film, electric field-induced trapping and optical detrapping experiment was carried out in working sample. The amount of carriers trapped per unit area was observed to be about  $10^{13}$  eV<sup>-1</sup>cm<sup>-2</sup>.

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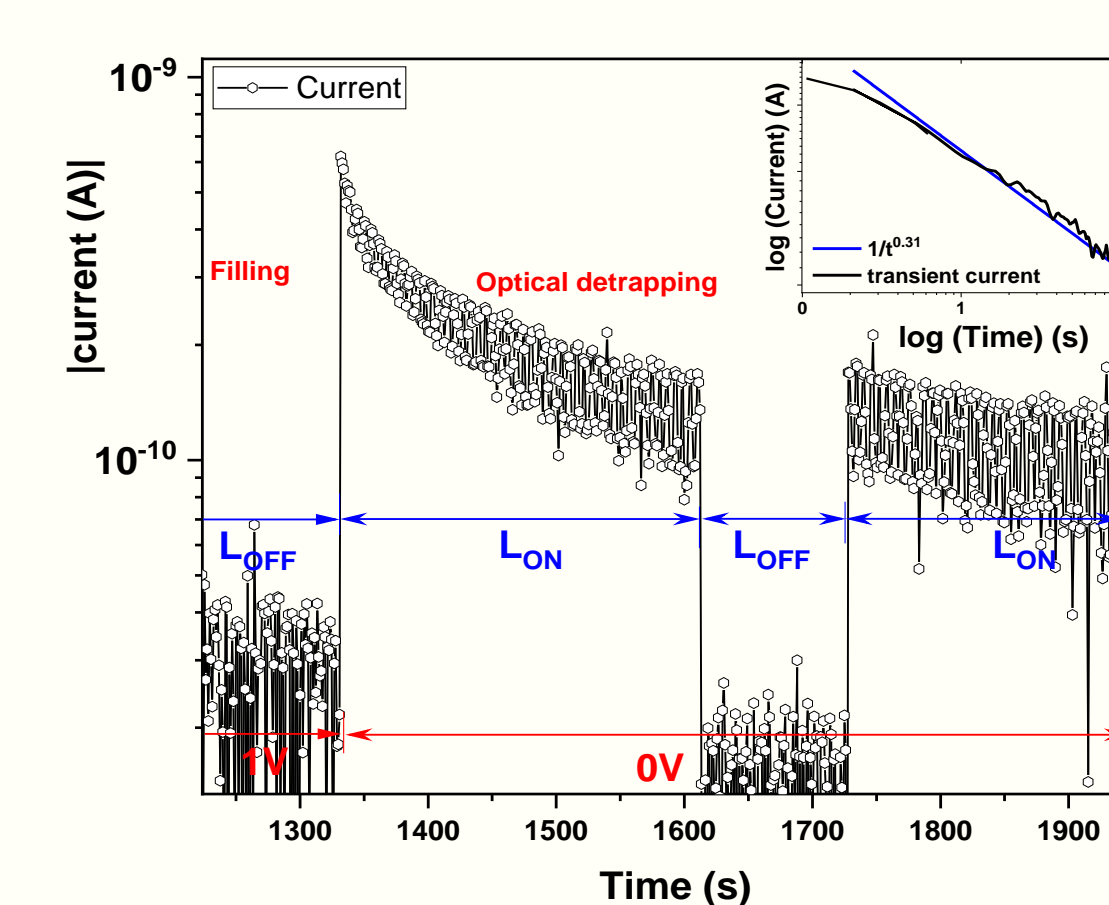
## Current response to the voltage



a) Write-read-erase-reread (WRER) cycles, b) Retention performance, c) Volatility test of memory device



ATR FTIR spectra measured at 25 °C, 100 °C and 150 °C during heating/cooling cycle.



Optical detrapping of trapped carriers: Electrically filled traps emptied using optical irradiation.

## Conclusion

- PCaPMA is a hole transporting polymer.
- ITO/PCaPMA/Al sandwich device showed two distinct bi-stable conducting states.
- High ON/OFF current ratio and acceptable retention ability.
- The nonvolatile memory effect is given by the filled traps and stabilization of extended conjugation formed by carbazole conformation supported by polymer networks via physical crosslinking with hydrogen bonds.