Supramolecular Control of Ionic Retention in Hybrid Bilayer Synaptic Transistors

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Principal Investigator(s): Yu Zhong
User(s): Haolei Zhou, Kaushik Chivukula, Qiyi Fang

Affiliation(s): Department of Materials Science and Engineering, Cornell University,

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Contact: yz2833@cornell.edu
Website: https://zhong.mse.cornell.edu

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Abstract:

The rise of big data and AI has exposed von Neumann architecture's limitations, spurring interest in computing paradigms that merge memory and processing. Artificial synapses, especially those based on electrolyte-gated transistors (EGTs) with ion-trapping layers, offer low voltage operation, robustness, and tunable retention. However, the molecular basis of ionic retention in these devices remains poorly understood.

Summary of Research:

Here, we report a supramolecular strategy to elucidate the molecular origin of ion retention in electrolyte-gated synaptic transistors. We designed a bilayer device comprising monolayer molybdenum disulfide (MoS_2) as the semiconducting channel and a polymeric ion-trapping layer incorporating dibenzo-18-crown-6 (DC), a cyclic host molecule known for its strong and size-selective binding to alkali metal ions (Fig. 1).1-2 Although crown ethers and their derivatives have been widely studied in ion recognition and transport, their potential to modulate ion retention dynamics in EGTs has been rarely explored.3-7 We fabricated the bilayer device using the following steps: To fabricate pre-patterned substrates, a 2-stage photolithography/e-beam deposition step was carried out on a 1 inch x 1 inch Si/SiO_2 piece to deposit source/drain electrodes and an SiO_2 insulating layer. Following this, we sequentially transfer a monolayer MoS_2 layer and DC-based thin film, thus yielding the final bilayer EGT device.

We show that ion retention in the DC layer is governed kinetically by ion concentration (Fig. 3) and thermodynamically by the competition between ion–host binding and ion solvation (Fig. 4), which can be tuned by solvent polarity. In particular, we demonstrate that the dielectric constant of the electrolyte plays a critical role in modulating the retention time, ranging from rapid ion relaxation to effectively permanent trapping within the crown ether layers. Experimental measurements and density functional theory (DFT) calculations reveal that these parameters reshape the free energy landscape of ion-DC binding versus solvation, thereby tuning the effective k1/k-1 ratio and controlling the rate of ion release. By selecting intermediate solvent conditions, we achieve memory retention dynamics suitable for emulating key short-term and long-term synaptic functions (Fig. 5).

Conclusions and Future Steps:

In conclusion, we constructed a bilayer EGT with a polymeric ion trapping layer to elucidate the molecular origin of ionic retention in such devices. Ion concentration and solvent polarity emerged as critical factors governing the kinetic and thermodynamic control of ionic retention. In particular, the solvent's dielectric constant played a pivotal role in modulating the balance between ion binding to crown ether units and ion solvation, leading to behaviors ranging from effectively permanent trapping to rapid ion relaxation. Intermediate solvent conditions allowed for the emulation of key short-term and long-term plasticity functions, thereby demonstrating a proof-of-concept neuromorphic device. These results highlight key strategies for controlling ion relaxation dynamics, providing valuable insights for the design of ionic–electronic artificial synapses.

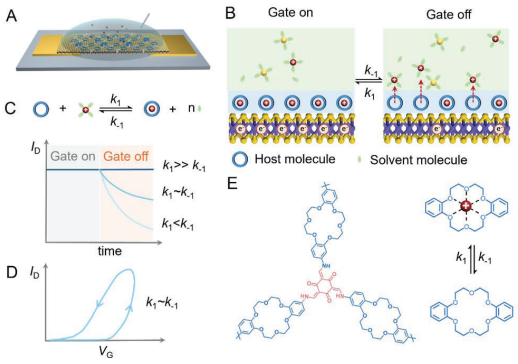

Figure 1: Working mechanism of the hybrid bilayer electrolyte-gated transistor.(A) Schematic of the bilayer transistor.(B) Illustration of ion capture/release in DCP film driven by gate-voltage.(C) A simplified schematic illustrating ion capture/release reaction rates (top), and the effect of these reaction rates on the dynamics of source-drain current (ID) (bottom). (D) Transfer characteristics of the bilayer transistor with comparable ion capture and release rates. (E) Structure of the ion trapping layer functionalized with 18-crown-6 building unit (left), and ion trapping/release reactions with crown ether units

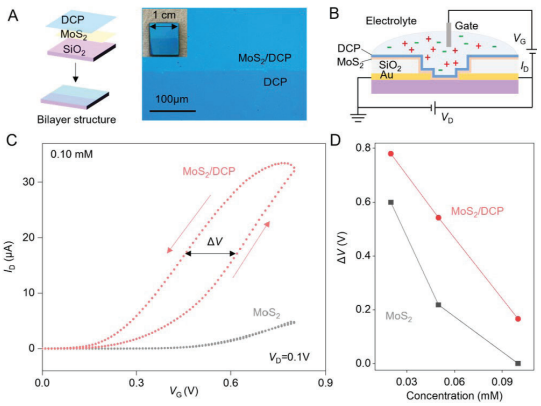

Figure 2: Electrical characterization of the hybrid bilayer electrolyte-gated transistor. (A) Schematic illustration of the stacking of bilayer structure (left) and optical image of the MoS2/DCP bilayer (right). Inset: Photo of the bilayer structure. (B) Schematic of the electrical characterization setup. (C) Transfer characteristics of the MoS2/DCP and MoS2 based transistors. (D) Hysteresis as a function of electrolyte concentration.

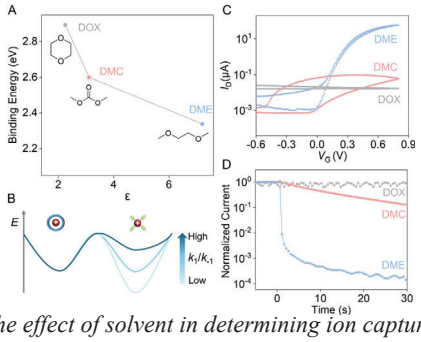

Figure 3: The effect of solvent in determining ion capture/release dynamics. (A)Ion-host binding energy as a function of the solvent's dielectric constant. (B) Energy diagram of the ion-interaction between host molecules and solvate molecules as a function of trapping dynamics. Effect of solvent on (C) the transfer characteristics of the bilayer transistor, and (D) Ion-retention dynamics measured in terms of normalized source-drain current after gate voltage application

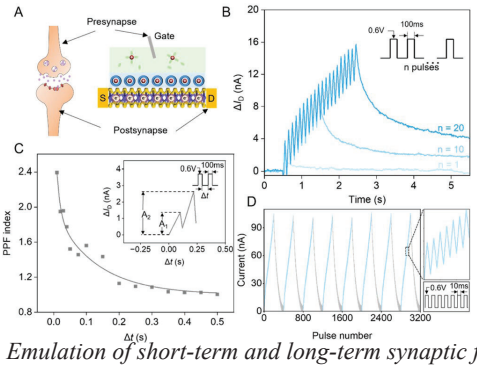

Figure 4: Emulation of short-term and long-term synaptic functions in the bilayer transistor. (A) Schematic illustration of the analogy between a biological neuron and the bilayer transistor (B) Short-term to long-term memory transition induced by the application of many gate pulses. (C) Paired pulse facilitation showing the relative magnitude of current increment as a function of the time-interval between two consecutive gate pulses. (D) Long-term potentiation and depression achieved by the application of a train of gate pulses.

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