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Article

Keywords:

Posted Date: January 20th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1156230/v1>

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Additional Declarations: There is **NO** Competing Interest.

Version of Record: A version of this preprint was published at Nature Materials on November 21st, 2022.
See the published version at <https://doi.org/10.1038/s41563-022-01402-2>.

Dynamic Molecular Switches Drive Negative Memristance Emulating Synaptic Behaviour

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Abstract: To realise molecular scale electrical operations beyond the von Neumann bottleneck, new types of multi-functional switches are needed that mimic self-learning or neuromorphic computing by dynamically toggling between multiple operations that depend on their past. Here we report a molecule that switches from high to low conductance states with massive negative memristive behaviour that depends on the drive speed and number of past switching events, with all measurements fully modelled using atomistic and analytical models. This dynamic molecular switch (DMS) emulates synaptic behaviour and Pavlovian learning, all within a 2.4 nm thick layer that is three orders of magnitude thinner than a neuronal synapse. The DMS provides all fundamental logic gates necessary for deep learning because of its time-domain and voltage-dependent plasticity. The synapse-mimicking multi-functional DMS represents adaptable molecular scale hardware operable in solid-state devices opening a pathway to simplify dynamic complex electrical operations encoded within a single ultra-compact component.

Introduction

Inspired by the energy efficiency of brains and the ever-increasing demand for miniaturised electronics, there is a drive to develop devices that mimic the dynamic character of neurons and synapses to create trainable, adaptive computing networks or new hardware for deep learning for various applications, including pattern recognition, classification, or to realise non-von Neumann neuromorphic computation¹⁻⁵. Neuromorphic computing revolves around emulating synaptic plasticity in electronic systems. Such operations are currently performed using complex, energy-inefficient silicon-based circuits with large footprints, or *mesoscale* memristive systems based on ferroelectric⁶ or phase change materials⁷, filaments, or migration of dopants^{1,3,8}. In this context, molecular switches are appealing because of their inherently small size but molecular switches so far are static, meaning they switch between fixed on and off states (*e.g.*, magnetic, redox, or conformational states)⁹⁻¹¹. Here we report a dynamic molecular switch in a tunnel junction that remembers its history, whereby the switching probability and the values of the on/off states continually change. This dynamic switch successfully emulates synaptic behaviour, Pavlovian learning, and, by exploiting the time-domain plasticity of the junctions, mimics all two-terminal logic gates necessary for deep learning. These functionalities are provided within a single molecular layer (2.4 nm thick), smaller than a neuron synapse (~1-10 μm) by at least three orders of magnitude, and thinner even than the synaptic gap (~20-40 nm) by an order of magnitude. This dynamic nature represents a new class of multi-functional molecular switch simplifying brain-inspired electronic devices, opening the door to neuromorphic computing at the molecular scale.

One of the goals of neuromorphic electronics is to produce computing systems where the training is done at the hardware level but molecular hardware for doing so

is not available. Unlike molecular switches studied so far, biological switches, *e.g.*, synapses, are inherently dynamic operating far away from thermodynamic equilibrium^{12,13} and therefore can be trained. In synapses (Fig.1a), information travels in the form of an action potential from a presynaptic neuron to a postsynaptic neuron through the synaptic gap, as regulated by the combined excitatory and inhibitory neural inputs¹⁴. By coupling different processes each characterised with different time constants, *e.g.*, fast depolarisation coupled to slow diffusion of Ca^{2+} and neurotransmitters, the synapses can be strengthened or weakened depending on their activity¹⁵ resulting in synaptic plasticity enabling pulse pair facilitation and depression with spike rate and timing dependent plasticity. To emulate the dynamical behaviour of synapses at the molecular level, we combined fast electron transfer (akin to action potentials and fast depolarisation processes) with slow proton coupling limited by diffusion (akin to the role of Ca^{2+} or neurotransmitters).

Solid-state dynamic molecular switches

Fig.1b-d shows the dynamic molecular switch (DMS) we introduce here, incorporated in junctions consisting of a self-assembled monolayer (SAM) supported by a gold bottom electrode in contact with an EGaIn top electrode. The SAM molecule has a 5,6,11,12,17,18-hexaazatrinaphthylene (HATNA) terminus that readily undergoes six successive proton coupled electron transfer (PC-ET) steps for dynamic covalent N-H bond formation^{16,17}. In the following we indicate the various oxidation states as $\text{H}_n\text{-HATNA}$ with $n=0-6$. When the molecules are oxidised ($n=0-2$) and turn on, electron transfer (ET) across the junctions is fast (fast channel, indicated by a blue arrow) resulting in a large increase of the currents flowing across the junction. In parallel to this fast ET process, proton addition steps occur, and N-H

formation slows down the ET rate (slow channel, dashed red arrow) and turns the junction off when HATNA is progressively reduced ($n=3-6$). In our experiments, water from the ambient (air, room temperature) is the proton source and so proton transfer is diffusion limited and much slower than ET. This switching from the fast to slow channel occurs at negative bias when the molecules are reduced resulting in a decrease of current and negative differential resistance (NDR). The junctions are oxidised back to their original states by applying a positive bias. Since the ET and proton coupling (PC) steps occur at very different time scales, our junctions can emulate the plastic behaviour of synapses, Pavlovian learning, and all logic gates, simply by changing the applied voltage and the duration of voltage pulses.

Fig.1. The dynamic molecular junction. **a**, Schematic of a synapse and the junctions **(b-d)**. The junction consists of a Au bottom electrode and EGaIn top electrode (EGaIn = eutectic alloy of gallium and indium). Solid and dashed blue arrows indicate electron transfer (ET) *via* coherent tunnelling through the fast and slow channels. The two ET channels are bridged by slow proton coupled electron transfer (PC-ET) where the protons are provided by water molecules in air.

Proton-coupled charge transport and dynamic covalent bond formation

We characterised the structure of the SAMs using various techniques (Methods and Supplementary Sections S2 and S3) and conclude that the SAMs are densely packed with all HATNA units confined to the top of the SAM as shown, for instance, by the molecular dynamics simulations (Fig.2a-c). To prove that the SAMs undergo sequential PC-ET *via* stable intermediates for reliable switching, we recorded a cyclic voltammogram (CV) from a S-C₁₀-HATNA SAM (Fig.2d). Four distinct redox waves are visible which is similar to the results by Ohsaka and co-workers¹⁷. They proposed that protonation initiates the first PC-ET step followed by ring-by-ring reduction of HATNA (Fig.2e) explaining why the PC-ET cascade appears as distinct redox waves. Our density functional theory (DFT) calculations confirm this mechanism (Supplementary Section S4).

Although the fully reduced SAM has essentially the same supramolecular structure as the SAM in its initial state (Fig.2c), our DFT calculations reveal that the electronic structure of the SAM strongly depends on the oxidation and protonation state of HATNA. Fig.2f shows projected density of states (PDOS) of the molecule during PC-ET following the steps in Fig.2g calculated with DFT. Fig.2g shows that the molecule in the initial state (H₀-HATNA) has large HOMO-LUMO gap (HOMO=highest occupied molecular orbital, LUMO=lowest unoccupied molecular orbital) of 2.1 eV, but upon initial protonation resulting in (HATNA)H⁺, a new mid-gap state appears around 1.1 eV above the Fermi-energy (E_F) of the Au electrode providing a low-energy tunnelling channel which defines the on-state of the junction (Figs. 1b and 2l-m). This state persists during the first two PC-ET steps resulting in H_n-HATNA with n=1,2 (Fig.1c) but then shifts towards lower energy before disappearing for H₅-HATNA and the large conductance gap is restored (Figs. 1d and

2o-p), turning the junction off (resulting in NDR as explained below). The changes in HOMO, LUMO, and mid-gap energy levels during all proton and electron addition steps are given in Fig.2g, Extended Data Fig. 1, and Supplementary Section S4.

Fig.2. Mechanism of Proton-Coupled Electron Transport. Representative computed structures of π - π driven supramolecular packing in S-C₁₀-HATNA SAMs on Au(111), from 0.1 microseconds of equilibrated room temperature molecular dynamics with H₀-HATNA shown from above (**a**) and from the side (**b**), and a zoom-in on H₆-HATNA shown from the side (**c**). Carbon, nitrogen, oxygen, sulphur, and hydrogen atoms are coloured cyan, navy, red, yellow, and white. (**d**) Cyclic voltammogram of a HATNA SAM on Au in contact with 2.0 M aqueous HClO₄ recorded at scan rate of 0.5 V/s showing four redox-waves labelled W1-4. **e** Proposed proton-coupled electron transport (PC-ET) mechanism. **f**, Calculated projected density of states (PDOS) on the molecule of HATNA SAMs on Au(111) for selected oxidation and protonation states (see Extended Data Fig. 1 for all states) and (**g**) the corresponding HOMO, LUMO and mid-gap energy levels for all states. The oxidation state is indicated by *n* and the protonation states are indicated by H⁺ (Supplementary Fig. S6). **h**, Heatmap of $\log_{10}|J|$ vs. V (24°C, relative humidity=60% in ambient conditions), and (**i**) Heatmap of $\log_{10}|J|$ vs. V measured under an atmosphere of compressed air with 10 ppm water. The black line is log-median average curve ($\langle \log_{10}|J| \rangle_m$ vs. V). **j**, Representative dataset with a fit to the theoretical model (fitting parameters given in Supplementary Table S10). **k-p**, Model of the dynamic switch. Energy level diagrams of the off (**k**, **n-p**) and on states (**l**, **m**) of the junctions where tunnelling is mediated by the acceptor level lying above E_F (blue bar), which is the LUMO at low negative or positive bias (**k-l**) when off-resonant tunnelling dominates but falls in the conduction window at elevated negative bias when the low-lying mid-gap state forms because of PC-ET (**m**). The rate equations describe coherent ET tunnelling (horizontal transitions) coupled to slow PC steps (vertical transitions). H₆-HATNA can be reset into H₀-HATNA by applying a positive V (**n**). PC increases the tunnelling barrier height of the ET channel by an interaction energy χ which decreases the molecule-electrode coupling strength γ by a factor κ (resulting in a broad LUMO) (**o**) resulting in NDR. The LUMO in the off state is energetically accessible only at large negative bias (**p**). Note: Although the DFT calculations in panels f and g suggest that the HOMO level is close in energy to E_F , the UPS data indicate that the HOMO level is 2.1 eV below the Fermi level of the Au electrode (Supplementary Section S3.2). Given the common problem of level alignment in DFT calculations¹⁸, we rely on the UPS data to properly position the levels with respect to the electrode work functions in our energy level diagrams shown in panels k-p.

Negative differential memristance

Fig.2h shows the $J(V)$ current density-voltage response from the Au-S-C₁₀-HATNA//Ga₂O₃/EGaIn junctions (see Methods for details). The large hysteric NDR peak can be explained by following the applied voltage in steps 1→4 as indicated. Step1: the voltage increases to +1.0 V which ensures the HATNA moieties are oxidised (*n*=0). Step2: voltage is reduced and around -0.9 V the current sharply increases as an empty molecular state enters the bias window and the mechanism of

charge transport changes from off (Fig.2k) to on resonant tunnelling (Fig.2l-m). The PDOS data indicate that the lowest available tunnelling level is the mid-gap state associated with (HATNA)H⁺, which is likely considering the basic nature of HATNA. Step3: with increasing negative bias, the junctions progressively turn on forming H_n-HATNA with n=1,2 (which have this mid-gap state), but turn off at large negative bias when molecules are reduced up to H_n-HATNA with n=5,6 (which lack the mid-gap state) resulting in reduction of current (Fig.2n-p) and consequential NDR. Step4: During retrace from -2 to 0 V, junctions remain in the off state resulting in large hysteretic NDR with a memory (*i.e.*, negative memristance). Only at positive bias, the H_n-HATNA moieties are oxidised to HATNA (n=0) when the HOMO falls inside the conduction window and the cycle restarts (Fig.2n). The value of R_{PIV} is 13.7 ± 3.5 (at 10 mV/s) and the value of $R_{on/off}$ is $2.64 \pm 1.41 \times 10^2$ which are the among the highest values recorded in molecular junctions¹⁹.

Theoretical model for NDR and dynamic switches

There are currently no *ab initio* theories available that can model the dynamical behaviour of junctions, but the analytical model developed by Migliore and Nitzan²⁰ captures all our observations as illustrated in Fig.2k-p in the form of energy level diagrams which were constructed based on our DFT (Fig.2f-g) and spectroscopy results (Supplementary Section S3.2). The model helps us identify the switching regimes in detail (as demonstrated previously for other switches²¹), and more importantly, establishes the mechanism of the time and applied-voltage dependency of the dynamical behaviour of the switching. The model describes simultaneous fast ET and slow PC processes in a molecular junction that lead to switching between fast and slow ET channels (Fig.1) as described in detail in Supplementary Section S6. No

molecular orbitals are available for charge transport at low bias (Fig.2l) but at intermediate negative bias (step 3, Fig.2h and Fig.2m) the mid-gap state enters the conduction window, increasing the ET rates of the on state (R_{AB} and R_{BA} defined in Fig.2l-m) after addition of one H^+ , *i.e.*, $H_0\text{-HATNA} \rightarrow (H_0\text{-HATNA})H^+$. This protonation step changes the tunnelling barrier height defined by the LUMO to that defined by the mid-gap state as indicated by χ (Fig.2o-p) and the molecule–electrode coupling strength (given by γ and factor κ). Thus, χ defines the mid-gap to LUMO energy difference which is 2.1 eV (Supplementary Section S6) in good agreement with DFT (1.5-2.0 eV, Fig.2g). At high bias, the HATNA moieties are progressively reduced and junctions turn off again which lowers the ET rates $R_{\overline{AB}}$ and $R_{\overline{BA}}$ (defined in Fig.2o-p) resulting in NDR. In parallel, PC (R_{+PC} and R_{-PC}) occurs at much slower rates than ET across both the fast and slow channels (*i.e.*, $R_{+PC} \ll R_{AB}, R_{\overline{AB}}$), but PC is responsible for switching. Therefore, the ET rates (R_{AB}, R_{BA} and $R_{\overline{AB}}, R_{\overline{BA}}$) and associated currents in the on (I^{AB}) and off ($I^{\overline{AB}}$) state are modelled with a single-level Landauer model²² while the much slower PC steps (R_{-PC}, R_{+PC}) are described by Marcus theory²³ routinely used to model PC-ET steps²⁴⁻²⁶. Following Migliore and Nitzan’s model²⁰, the current that flows across the junctions is calculated from the probability of the junctions to be in the on (P^{AB}) or off ($P^{\overline{AB}}$) state as given by

$$I(V) = P^{AB}(V)I^{AB}(V) + P^{\overline{AB}}(V)I^{\overline{AB}}(V) \quad (Eqn1)$$

where $P^{AB}(V) = 1 - P^{\overline{AB}}(V)$. The overall dynamical probability of the junction is governed by the slow protonation rates $\langle R_{+PC} \rangle$ and $\langle R_{-PC} \rangle$

$$\frac{dP^{AB}}{dt} = (1 - P^{AB}) \langle R_{+PC} \rangle - P^{AB} \langle R_{-PC} \rangle \quad (Eqn2)$$

Fig.2j shows a fit of this model to the $J(V)$ data and reproduces all important observations: NDR, hysteretic switching, and the reset at positive bias (which

involves the HOMO, Fig. 2k, n) (Supplementary Section S6). This modelling of the junction successfully describes the behaviour as shown by Figures 2j, 3a and 3g and confirms that the appearance and disappearance of the mid-gap state causes switching and gives feedback on how and when the protonation occurs by giving an estimate for the switching probability (Fig.3g). To demonstrate that the presence of water is important, we repeated the experiment with relative humidity <5% where no NDR effect is found (Fig.2i).

Emulating synaptic behaviour

To demonstrate basic synaptic function with our junctions, we perform pulse-pair facilitation (PPF) and depression (PPD) as follows. Fig.3a shows a typical pulse-pair sequence and current response. The difference in chordal conductance ($G=I_{\text{bias}}/V$) between the measured and reference pulse in the pair, divided by the chordal conductance of the reference pulse, $\Delta G/G$, is used to quantify PPF and PPD, along with a modelled current response (more detail given in Supplementary Section S5.2). The magnitude of the voltage pulse (V_p), pulse duration (t_p), and time delay between consecutive pulses (t_d), programme the junction. For instance, Fig.3b shows that by changing V_p (with $t_p=t_d=1$ s) both conductance enhancement (excitatory potentiation) and depression (inhibitory potentiation) are obtained (Extended Data Fig. 2). Fig.3c shows that the extent of the potentiation depends on t_p where $\Delta G/G$ follows an exponential decay with characteristic time 2.4 ± 0.9 s (Extended Data Fig. 3 and Supplementary Section S5.2.1.2).

Changing the delay between pulses provides different programming schemes. No significant decay is found in delays over minutes if the voltage is set at 0 V (Supplementary Section S5.2.1.3). However, the delay voltage can be set to a positive

value, *i.e.*, reset voltage V_r , so that the junction will reset over time. Fig.3d shows that by changing t_d (with $V_p=-2.0$ V and $t_p=1$ s) the conductance decreases exponentially with characteristic time of ~ 2.5 s (Extended Data Fig. 4 and Supplementary Section S5.2.1.2). The speed of this reset process can be adjusted through the magnitude of V_r (Fig.3e and Extended Data Fig. 5). Fig.3d shows that spike timing dependent plasticity (STDP), where the order in which the pulses are applied and the delay between them modulates $\Delta G/G$, can also be emulated (Supplementary Section S5.2.1.2). The characteristic decay times of 12 s for positive t_p and 7s for negative t_p are consistent with values obtained from our model (24s and 8s respectively). Spike rate dependent plasticity (SRDP) is shown in Fig.3f. A negative inhibitory pulse ($V_p = -1.0$ V) is applied at a set frequency while a positive excitatory voltage ($V_d = 1.25$ V) is sustained during the delay between these pulses. Depending on the rate of the inhibitory pulse, the junction can have a net excitatory (46 mHz) or inhibitory (250 mHz) evolution over successive periods. These results demonstrate that, as in biological neural systems^{27,28}, the frequency of the signal decides the (synaptic) junction response. This rate control provides a way to create discrete conductance states that can be recognised in subsequent cycles using several regular pulses. Fig.3g shows that junctions successfully reproduce discretisation of ten conductance states; this behaviour could be fully modelled. Repeated identical pulses do not potentiate the junction in a constant manner, instead the junctions show habituation, *i.e.*, the junction desensitises to the signal as the response decays exponentially (as indicated in Fig.3f), mimicking how biological systems avoid overstimulation²⁹. This habituation can be reversed through reset pulses and can be explained by the finite number of molecules electrically active in the junction, as captured by the model.

Fig. 3. Synaptic function. **a**, Typical voltage paired-pulse sequence and current response used to extract PPF and PPD properties, as measured (blue line) and modelled (red line) (additional fits are given in Supplementary Section S6.3). **b-e**, $\Delta G/G$ as a function of: **(b)** $-V_p$, **(c)** t_p , and **(d)** t_d with exponential fits (solid lines) used to extract characteristic time constants (Supplementary Sections S5.2.1.2 and S6.3), **(e)** V_r , with dashed black lines as a visual guide. The pulse sequences and $I(V)$ profiles of the junctions used are shown in Extended Data Figures 2-5. **f**, Pulse sequence exhibiting SRDP with $V_p = -1V$ at 46mHz or 250mHz with the inter-pulse delay at $V_d = 1.25V$. The solid black arrows indicate the effects of habituation. **g**, Identification and retrieval of conductance states over successive cycles and fit to the model. Dashed black lines are visual guides to show the recovery of the first four conductance states. The lower panel shows the evolution of dynamical switching probability P .

Emulating Pavlovian learning and logic gates

The junctions can be incorporated in electrical artificial neural networks (e-ANNs). Fig.4 shows an e-ANN that mimics Pavlov's experiment demonstrating the potential for the synapse to serve as a basis for Hebbian learning, *i.e.*, training of an input by simultaneous operation with another input ('neurons that fire together, wire

together'¹⁴). Two inputs are fired from neurons N1 and N2 (here sources of voltage pulses) through synapses (electronic junctions) S1 and S2 respectively, to output neuron N3 (an ammeter), as shown in Fig.4a. In the Pavlov analogy, N1 represents '*dog sees food*' which readily delivers an output in N3 '*dog salivates*' (Fig.4b). The sensitised synapse S1 between the two is materialised by a low-resistance resistor in the circuit. On the other hand, N2 (or '*dog hears bell*') does not readily deliver the output in N3 (see insignificant output in Fig.4c, '*dog does not salivate*'), but can be trained to do so through simultaneous operation of N1 and N2 (Fig.4d, '*dog sees food and hears bell*'). This sensitises the adaptive synapse S2 (the dynamic switch) and subsequently enables N2 to produce an output in N3 (Fig.4e) (Extended Data Fig. 6). In this set-up, the whole Hebbian learning functionality is provided by the DMS, without the use of a third terminal and additional relays as reported before³⁰.

Components that can perform logic can be used as hidden layers in hardware deep-learning systems³¹. The time-domain plasticity of the DMS can be used to emulate all standard Boolean logic gates. While the DMS is a two-terminal component and standard logic gates require at least two inputs for one output, the time-domain plasticity of the DMS makes it possible to consider an applied voltage pulse as two separate inputs by separating the voltage and time domains in the pulse. The voltage magnitude of the pulse is one input and its duration a second input, and the resulting modulation in the conductance of the junction represents the output: positive if excitatory, and negative if inhibitory (Fig.4f-g). By defining the input states V_{on} , V_{off} , t_{on} , t_{off} , the DMS can provide all the fundamental logic gates as shown in Fig.4h-I and Extended Data Fig. 7 (Supplementary Section S5.2.3).

Fig.4. Demonstration of Pavlovian learning and Boolean logic gates using time plasticity in the DMS. **a**, Schematic of the electrical circuit. Two input neurons N1 and N2 are connected to an output neuron N3 via synapses S1 (resistor) enabling strong coupling between N1 and N3, and S2 (DMS), the trainable synapse. **b-e**, Pulse sequences showing Pavlovian learning. **b**, Pulse sequence representing ‘dog sees food’, pulses from N1 produce a strong output in N3. **c**, ‘dog hears bell’ before training, N2 produces an insignificant output in N3. **d**, ‘dog sees food and hears bell’, which trains S2. Pulses from N1 and N2 combined produce a strong output in N3. **e**, ‘dog hears bell’ after training, N2 now produces a significant output in N3. **f**, A reference voltage pulse is followed by the logic pulse to perform the operation and finally a read-out pulse. **g**, The current read-out pulse is compared to the reference pulse, where current increase is defined as output=1 and current decrease as output=0. Demonstration of the AND (**h**) and OR (**i**) logic gates. All other gates and input parameters are shown in Extended Data Fig. 7 and Supplementary Section S5.2.3.

Conclusions

We report a dynamic molecular switch (DMS) of just 2.4 nm that readily emulates the plasticity of synapses, exhibits Pavlovian learning, and can be configured to perform all logic gates required for deep learning, all within one junction. This multifunctionality combined with reconfigurability has the potential to simply brain-inspired electronic devices considerably. The switching probability of the junction changes dynamically between high and low conduction states enabled *via* PC-ET

driven dynamic N-H bond formation. A challenge is usually to understand the microscopic origin of the dynamics of mesoscale artificial synapses, and such systems are usually modelled with equivalent circuit analysis or network models. In contrast, the dynamical behaviour of our DMS can be readily captured with intertwined rate equations with different time constants and can be applied to dynamic molecular systems driven by other stimuli (such as light³²) and coupled to different types of dynamic covalent bond formation³³ opening up a whole new range of adaptive and reconfigurable systems with orthogonal inputs and outputs.

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Methods

Synthesis. 5,6,11,12,17,18-hexaazatrinaphthylene (HATNA) was synthesised following the similar procedure reported previously³⁴, the detailed synthesis scheme and characterisation of molecule are summarised in Supplementary Section S2.

Electrode preparation. The cone-shaped GaOx/EGaIn top-electrode was formed using previously reported methods³⁵. The gold bottom-electrode was prepared following reported template stripping methods³⁶. We deposited 200 nm thick Au films (containing 99.999% Au granules, ACI Alloys) on commercial Si (100) wafers (with a native SiO₂ thin layer on surface) using a Shen Yang Ke Yi thermal evaporator. Clean glass slides were then glued onto the Au surface with thermal glue (EPOTEK 353ND) and cured at 80 °C for 3 hours. To minimise contamination from the atmosphere, the wafers coated with Au were stored in a dry box and the Au was template-stripped immediately before use.

Self-assembled monolayer (SAM) formation on Au^{TS}. The S-C₁₀-HATNA SAMs were formed using well-established methods³⁵. Typically, 1.0 mg HS-C₁₀-HATNA was dissolved in freshly distilled THF (6 ml) to obtain a solution with a concentration of 0.2–0.3 mM. The solution was degassed for 15 min with N₂ to remove oxygen, and then a freshly template-stripped Au surface was immersed into the solution for 24 h under an atmosphere of N₂. The coated Au substrates were then removed from the solution and washed with THF and ethanol to remove physisorbed molecules and gently dried in a flow of N₂.

Electrochemistry. The S-C₁₀-HATNA SAMs on Au were electrochemically characterised by cyclic voltammetry. We used a custom-built electrochemical cell equipped with a Pt counter electrode, Ag/AgCl reference electrode and Au^{TS} working electrode. A HClO₄ aqueous solution (2M) was used as the electrolyte, similar to a previous report¹⁷. The cyclic voltammograms were recorded between -0.3 V and 0.8 V at scan rates ranging from 0.05 V/s to 10 V/s with an Autolab PGSTAT302T equipped with NOVA 1.10 software (Supplementary Section S3).

Surface characterisation. Synchrotron-based photoemission spectroscopy, including X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy were performed using the Surface, Interface and Nanostructure Science (SINS) beamline of the Singapore Synchrotron Light Source (SSLS). The experimental procedures are described in our previous work³⁷. We measured the SAMs of S-C₁₀-HATNA on template-stripped Au surfaces. For high-resolution XPS, we used photon energies of 350 eV for S 2*p* and C 1*s*, 600 eV for N 1*s* and 650 eV for O 1*s* spectra for optimal photoionisation cross-sections at these core-levels. We recorded each XPS signal with two different photoelectron take-off angles, 90° (normal emission, NE) and 40° (grazing emission, GE). We performed peak fitting using *pseudo*-Voigt functions with a fixed 70% Gaussian and 30% Lorentzian ratio and a Shirley background. The detailed results of surface characterisation were shown in Supplementary Section S3.

DFT electronic structure calculations. We calculated the density of states (DOS) distributions for the HS-C₁₀-HATNA and the reduced state HS-C₁₀-(H₆-HATNA) and all intermediate states along the PC-ET path using previously reported methods³⁸. All

computed reorganisation energies of HATNA during sequential PC-ET steps, the calculated PDOS of Au-S-C₁₀-HATNA and post-PCET Au-S-C₁₀-(H₆-HATNA), the computed surfaces of the electron acceptor mid-gap and LUMO→LUMO+2 levels, and the calculated PDOS on the molecule of HATNA SAMs on Au(111) for all intermediate oxidation and protonated states are summarised in Supplementary Section S4.

Junction fabrication and electrical measurements in air. We formed electrical contacts to the SAMs with cone-shaped tips of GaOx/EGaIn using previously reported methods³⁵. All measurements were performed with the bottom contact connected to the ground and the bias was applied to the EGaIn top electrode from 0 V → +1 V → 0 V → -2 V → 0 V. A Keithley 6430 source meter was used to bias the junction controlled by LabVIEW. The $J(V)$ curves were recorded in steps of 20 mV (Supplementary Section S5).

Statistical analysis of $J(V)$ characteristics. All $J(V)$ data were used to perform the statistical analysis excepting the unstable and shorted junctions. We define a junction as unstable when the current value suddenly increased to the compliance limit of our electrometer. The number of consecutive $J(V)$ traces is limited to 3 traces per junction because of the memory effect on the switching probabilities of the molecules (as explained in the main text). We determined the median averages of the values of $\log_{10}|J|$ along with the median absolute deviations, σ_m , a recommended alternative method as described in ref³⁹, because this method does not rely on assumptions regarding the distribution of the data. From all $\log_{10}|J|$ values measured at each bias, we calculated the median $\log_{10}|J|$ average, $\langle \log_{10}|J| \rangle_m$, and σ_m . We created our

heatmaps using 2D kernel density estimations with OriginPro 2019b. We used exact estimation as the density calculation method, bivariate kernel density estimator as bandwidth selection method and a grid size of 100. Exact estimation method in OriginPro 2019b calculates the density values based on a bidimensional Gaussian kernel. See the detailed description in Supplementary Section S5.

Synaptic behaviour, Pavlovian learning, and logic gates. The measurements of the junctions as an artificial synapse were carried out with samples prepared using methods as described in the SAM formation section in the Methods and using a cone-shaped tip of GaOx/EGaIn as described in the Electrodes preparation section in the Methods. For each junction an initial $I(V)$ measurement was performed as described in the Junction fabrication and electrical measurements section in the Methods to ensure the junction had $J(V)$ characteristics close to the log-median (Fig. S7), as given in Supplementary Information Section S5.2. Following this, sequences of voltage pulses were programmed and applied using LabView-based software CryoMeas (developed by Prof C.J.B. Ford, University of Cambridge) using a Keithley 6430 source meter which recorded the current simultaneously. A typical pulse sequence used to extract plasticity depending on pulse parameters is shown in Fig. 3a, while the custom pulse sequences used for Pavlovian learning are shown and described in Supplementary Information Section S5.2. Pavlovian learning was demonstrated in a set-up involving two Keithley 6430 source meters operated simultaneously as described in the main text (Fig. 4a-e) and Extended Data Fig. 6 Supplementary Information Section S5.2.2. Pulse parameters used for the logic gates are described in Supplementary Information Section S5.2.3.

Theoretical Modelling of the Transport Dynamics. We have used a theoretical model developed by Migliore and Nitzan²⁰ to model the junction characteristics and explain our observations. We used the standard single-level quantum model to account for the current through the molecular junction in both the on and off states which has been shown to effectively describe the conduction through single-molecule junctions, which has been modified by us to describe the current across large-area molecular junctions^{35,40}. The model described above has been used to fit the data presented in Figs. 3d-h in the main text. The detailed description of the mechanistic modelling, Landauer formalism to account for the tunnelling in the on and off states, fitting of the data and the related discussion are given in Supplementary Section S6.

Data availability: Data and codes are available in the supplementary materials and on <https://dataverse.harvard.edu/privateurl.xhtml?token=efd1a016-cc24-41ab-891b-5217fa6dd56d>.

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ACKNOWLEDGEMENTS

We thank the Ministry of Education (MOE, Award No. MOE2018-T2-1-088 and MOE2019-T2-1-137) and the Prime Minister’s Office, Singapore, under its Medium Sized Centre program for supporting this research. D.T. acknowledges support from Science Foundation Ireland (SFI) under awards number 15/CDA/3491 and 12/RC/2275_P2 and supercomputing resources at the SFI/Higher Education Authority Irish Center for High-End Computing (ICHEC). E.d.B. and C.N. acknowledge support from the U.S. National Science Foundation (Grant no. ECCS#1916874). D.Q. acknowledges the support of the Australian Research Council (Grant No. FT160100207).

Author contributions

C.A.N. conceived and supervised the project. D.T. conducted the atomistic modelling. E.d.B. and C.N. conducted the numerical modelling. Y.W. synthesised the compounds, Y.W. and Y.H. performed the CV and UV–vis measurements. Z.Z. and

D.Q. performed the AR-XPS and NEXAFS measurements and analysis. Y.W. and Q.Z. performed the I - V electrical measurements. H.P.A.G.A. designed, performed and analysed the synaptic emulation measurements. A.L. developed the Origin code for electrical data analysis. C.A.N., E.d.B., D.T., and H.P.A.G.A. wrote the manuscript and all authors commented on it.

Competing interests: The authors declare no competing interests.

Additional information

Extended data is available for this paper at <https://doi.org/xxx>.

Supplementary information is available for this paper at <https://doi.org/xxx>.

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Extended Data

Extended Data Fig. 1. The periodic DFT calculations. **a**, The calculated PDOS of Au-bound S-C₁₀-HATNA with the nitrogen sites plotted as a thick black line. The full molecule is shown as a dashed grey line and contributions from carbon, hydrogen, oxygen, and sulphur sites are plotted as green, red, purple, and blue lines, respectively. **b**, The calculated PDOS of post-PCET Au-S-C₁₀-(H₆-HATNA). **(c)** Computed surfaces of the empty electron-acceptor LUMO $\rightarrow$ LUMO+2 levels in Au-S-C₁₀-HATNA together with the mid-gap state created at +1.1 eV in the first protonation step generating Au-S-C₁₀-H⁺-HATNA. **d**, The calculated PDOS on the molecule of HATNA SAMs on Au(111) for all oxidation and protonated states.

Extended Data Fig. 3. Measurement of potentiation as a function of negative pulse duration as shown in Fig. 3c. **a-b**, $I(V)$ profile of the junction used in the measurement in linear (**a**) and logarithmic scale (**b**). **c-e**, pulse sequence used in the measurement with current (**c**), logarithm of current (**d**) and voltage (**e**) as a function of time, with colour used to help distinguish sections of the sequence. A first negative voltage pulse of amplitude $V_p = -2\text{V}$ and duration t_p was applied, a delay at 0V was set for $t_d = 1\text{s}$, a second negative voltage pulse of magnitude V_p was applied, followed by a series of positive voltage pulses of amplitude $V_r = 1.25\text{V}$ to reset the junction. This sequence was repeated each time varying V_p the amplitude of the negative voltage pulses from 0.5V to 2V and back, and after half a sequence to train the junction, the current amplitude of the second negative pulse was compared to that of the first negative pulse to determine the potentiation as a function of V_p .

Extended Data Fig. 5. Measurement of potentiation as a function of positive pulse duration as shown in Fig. 3e. **a-b**, $I(V)$ profile of the junction used in the measurement in linear (**a**) and logarithmic scale (**b**). **c-e**, pulse sequence used in the measurement with current (**c**), logarithm of current (**d**) and voltage (**e**) as a function of time, where colour is used to help distinguish sections of the sequence. A negative reference voltage pulse ($V_p = -1.5$ V, $t_p = 1$ s) was applied, a positive voltage pulse of varying amplitude (duration $t_d = 2$ s) was applied, and a second negative voltage pulse ($V_p = -1.5$ V, $t_p = 1$ s) was applied. This sequence was repeated each time varying V_r the amplitude of the positive voltage pulse from 0.5 V to 2 V and back, and after one training sequence (~ 500 s), the current amplitude of the second negative pulse was compared to that of the reference negative pulse to determine the potentiation as a function of V_r .

Extended Data Fig. 6. Measurement demonstrating the Pavlov experiment (Hebbian learning). **a-b**, $I(V)$ profile of the junction used in the measurement in linear (**a**) and logarithmic scale (**b**). **c**, pulse sequence showing Hebbian learning (from Fig. 4b-e). The e-ANN works as follows: two source-measure units represent two artificial neurons N1 and N2 delivering voltage inputs in separate channels feeding into a third channel (see Fig. 4a) N3 where the current received is the output. N1 is connected via a fixed resistor ($1\text{k}\Omega$) to N3 and gives the output unconditionally. N2 includes the junction in the off state such that pulses from N2 do not initially result in a significant signal in N3. It corresponds to ‘dog hears bell’. However, firing pulses in N1 and N2 results in a PPF process in N2, ‘training’ it to deliver an output in N3 when pulses are fired from N2 thereafter. The sequences of voltage pulses are as follows. N1 alternates between pulses at -1 V and -1.1 V , each lasting 2 s , repeated 5 times. N2 alternates between pulses at $+1.5\text{ V}$ and -1.1 V , each lasting 2 s , repeated 5 times. When pulses are applied from N1 and N2 simultaneously, the voltage across the dynamic switch can be estimated to be alternating between $+2.4\text{ V}$ and -0.1 V approximately, according to Kirchhoff’s circuit laws, which excites the junction (enhances its conductance) and thus the coupling to N3.

Extended Data Fig. 7. Demonstration of remaining logic gates: **a**, XOR; **b**, NAND; **c**, NOR; **d**, NXOR, as per the operation system described in the main text and Fig. 4, with current and voltage traces and truth tables. More details on the pulse parameters are given in Supplementary Information Section S5.2.3.

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