Tunable Intervalence Charge Transfer in Ruthenium Prussian Blue Analog Enables Stable and Efficient Biocompatible Artificial Synapses

Donald A. Robinson, Michael E. Foster, Christopher H. Bennett, Austin Bhandarkar, Elizabeth R. Webster, Aleyna Celebi, Nisa Celebi, Elliot J. Fuller, Vitalie Stavila, Catalin D. Spataru, David S. Ashby, Matthew J. Marinella, Raga Krishnakumar, Mark D. Allendorf, and A. Alec Talin*

Emerging concepts for neuromorphic computing, bioelectronics, and brain-computer interfacing inspire new research avenues aimed at understanding the relationship between oxidation state and conductivity in unexplored materials. This report expands the materials playground for neuromorphic devices to include a mixed valence inorganic 3D coordination framework, a ruthenium Prussian blue analog (RuPBA), for flexible and biocompatible artificial synapses that reversibly switch conductance by more than four orders of magnitude based on electrochemically tunable oxidation state. The electrochemically tunable degree of mixed valency and electronic coupling between N-coordinated Ru sites controls the carrier concentration and mobility, as supported by density functional theory computations and application of electron transfer theory to in situ spectroscopy of intervalence charge transfer. Retention of programmed states is improved by nearly two orders of magnitude compared to extensively studied organic polymers, thus reducing the frequency, complexity, and energy costs associated with error correction schemes. This report demonstrates dopamine-mediated plasticity of RuPBA synapses and biocompatibility of RuPBA with neuronal cells, evoking prospective application for brain-computer interfacing.

1. Introduction

Mixed valence compounds (MVCs) that accommodate facile ion insertion and extraction have recently garnered intense interest for applications beyond energy storage such as neuromorphic computing, thermal and magnetic switching, and electrocatalysis.[1] This interest is motivated by the possibility to tune the electronic structure of the host via the coupled ion/electron insertion/extraction reactions characteristic of electrochemical charge transfer. Among the various classes of MVCs, the continually growing family of Prussian blue analog (PBA) coordination frameworks[2] stand out due to their high (electro)chemical stability,[3] fast ionic transport,[4] biocompatibility and applications for biosensing,[5] process compatibility with electron and photolithography,[6] high electrocatalytic activity,[3a,b] and synthetic tunability.[2b,c] However, fundamental insight into the electronic conduction mechanism remains limited for most PBAs,[7] including the archetypal Prussian Blue (PB),[8] thus hindering their utilization for electronics applications. The lack of PBA research in electronics is surprising, given the success of electron transfer theory in explaining the electronic properties of many mixed valence coordination compounds,[9] including cyanide-bridged polynuclear complexes that mimic the molecular building blocks of PBAs.[10] Polynuclear Ru-based mixed valence complexes are of particular interest because their degree of electronic delocalization lies within the “localized-to-delocalized” transition regime,[11] whereas Fe-based derivatives typically exhibit a more localized electronic structure. Ruthenium hexacyanoruthenate, a Ru-based PBA, is selected as the PBA of focus in this study because RuPBA is expected to have the largest range of tunable electronic conductivity as a function of valence state, due to its greater degree of charge delocalization in comparison to other PBAs. RuPBA is also a new material; only one prior report of the compound can be found in the literature, which focused on synthesis and characterization of the as-synthesized valence state.[12] Spectroscopic and electrical characterization of as-synthesized RuPBA indicated a more delocalized electronic structure as compared to PB.
The present investigation primarily focuses on exploring the relationship between electronic conductivity and electrochemically tunable valence state in a coordination framework, using RuPBA as a first example. The practical motivation for this study is to explore new materials for electrochemical random-access memory (ECRAM) devices\textsuperscript{[3]} with target applications in neuromorphic computing\textsuperscript{[14]} and brain-computer interfacing.\textsuperscript{[15]} The basic design principle for an ECRAM device is to hybridize a rechargeable battery with an electrochemically tunable transistor to make a three-terminal gate/source/drain nonvolatile memory device that translates multiple states of charge to multiple nonvolatile conductance states. Similar to electrochemical transistors, volumetric electrochemical charging of the gate/electrolyte/channel cell causes the bulk conductivity of the channel material to switch. Unlike typical electrochemical transistors, the gate of an ECRAM device is also composed of a battery material, which allows the newly switched conductance state to remain for long periods of time. This nonvolatile switching function of ECRAM enables long-term synaptic plasticity, a critical synaptic process for memory in living organisms.

In this report, RuPBA ECRAM devices are inkjet-printed on flexible substrates, biocompatible with neuronal cells, and can be switched to different nonvolatile conductance states by reaction with dopamine (DA). We elucidate the interrelationship between the electronic conductivity and the electrochemically tunable rate of intervalence charge transfer (IVCT) using Marcus-Hush theory (MHT),\textsuperscript{[16]} Boltzmann transport theory, and operando absorption spectroscopy, indicating that hole mobility greater than 1 cm\(^2\) V\(^{-1}\) s\(^{-1}\) is achievable in this material. Application of MHT to the absorption spectra at different oxidation states reveals that electronic conduction predominantly occurs through a cross-pore (CP) charge transfer pathway between N-coordinated Ru sites, consistent with density functional theory (DFT) predictions. To our knowledge, the RuPBA represents the first practical alternative material to conductive organic polymers and metal chalcogenides for neuromorphic devices based on ECRAM, offering promising avenues for innovation via the distinct ion/electron conduction mechanism and large synthetic flexibility of the PBA family of compounds.

2. Results and Discussion

2.1. Transfer Characteristics of Li/RuPBA ECRAM Device

Figure 1a shows the idealized structure of RuPBA, depicted without [Ru(CN)\(_6\)]\(^{3+}\) vacancies for simplicity, containing lithium ions intercalated within the square faces\textsuperscript{[7]} of the cubic CN-bridged cages. The as-synthesized RuPBA contains 3 at\% of K\(^+\) ions (Ru:K = 2.5:1), indicating that most of the Ru centers initially have a 2\(^+\) formal oxidation state. We expect the K\(^+\) ions exchange with the Li\(^+\) ions after the silica-based Li\(^+\)-containing ionogel electrolyte\textsuperscript{[38]} layer is printed over the RuPBA layer. The transfer curve in Figure 1c shows electrochemical tuning of the channel conductance (\(G\)) from a lower limit of \(\approx 9 \times 10^{-8}\) S to an upper limit of \(\approx 2 \times 10^{-4}\) S. Based on the RuPBA film conductivity in the as deposited state (\(4 \times 10^{-4}\) S cm\(^{-1}\), see Section S1, Supporting Information) and the measured conductance from Figure 1c (\(2 \times 10^{-5}\) S at \(V_{gd} = 0\) V), the electrochemically tunable conductivity range extends from \(\approx 10^{-6}\) to \(10^{-2}\) S cm\(^{-1}\). Interestingly, the lower conductivity at the fully reduced (fr) RuPBA (fr-RuPBA) state (\(\approx 10^{-6}\) S cm\(^{-1}\)) is close to that obtained by Xidis and Neff for fr-PB (\(5 \times 10^{-7}\) S cm\(^{-1}\)).\textsuperscript{[8]} We attribute the lower conductance limit at \(V_{gd} \approx 0.6\) V to that of fr-RuPBA, where all Ru centers have a 2\(^+\) formal oxidation state and the structure contains the maximum amount of lithium ions. Partial oxidation of fr-RuPBA causes Ru\(^{II/III}\) mixed valency and conductivity to increase.

Most of the accumulated electrochemical gating charge should be proportional to the amount of Ru\(^{II}\) species oxidized according to Faraday’s law, and thus should also scale linearly with the charge carrier concentration. Analysis of the transferred data shows a voltage range where the conductance changes linearly with accumulated gate charge (Figure S2, Supporting Information). The trend suggests that only carrier concentration changes in the linear region, while mobility remains constant. Outside of this region, oxidation of the RuPBA channel either causes the mobility to increase (0.6 V \(\leq V_{gd} \leq -0.1\) V) or decrease (\(-0.3\) V \(\leq V_{gd} \leq -0.6\) V). Upon oxidizing the channel further, the conductance decreases (Figure S3, Supporting Information). On the reverse scan from \(-1\) V to 0.6 V, the conductance increases to a maximum again during lithiation and then decreases as the channel is further lithiated, indicating that a mixed valence form is the most conductive.

2.2. Evaluation of ECRAM Device Performance

2.2.1. Long-Term Synaptic Plasticity

Linearity: Consistent with the transfer characteristics (Figure 1c), the voltage-controlled pulsed programming of an ECRAM device with a 0.75 ms “write” pulse duration shows that the long-term synaptic potentiation (G\(^\uparrow\)) and depression (G\(^\downarrow\)) ramps (Figure 2a) are highly linear, which is desirable for high accuracy during training.\textsuperscript{[14a,b]} (See also Figure S7, Supporting Information). The conductance range of 80–160 nS in Figure 2a corresponds to a read current range of 8–16 nA at the applied read voltage (\(V_r = 0.1\) V). The combination of low current and near-linear conductance tuning is ideal for energy-efficient programming.\textsuperscript{[14a]}

Devices fabricated with a proton-conducting polymer-based ionogel electrolyte (instead of Li\(^+\) electrolyte) show better switching behavior in terms of linearity and symmetry, but switch more slowly, requiring more than tenfold longer write pulse durations and twice as many pulses to cycle over a range of \(G_{max} = 2G_{min}\) (Section S4, Supporting Information).

Long-Term State Retention: State retention is essential for nonvolatile synaptic memory. As shown in Figure 2b, the programmed conductance over the entire range, 0.65–2.0 \(\mu\)S (\(G_{max}/G_{min} = 3\)), has a retention time of \(\approx 600\) s (defined as \(dG < 1\%\)). The loss in retention at \(G > G_0\) in Figure 2b indicates that the more oxidized RuPBA states are less stable than the reduced states. However, the conductance remains stable within \(\pm 1\%\) over a duration of \(\approx 10^4\) s for the range below the initial state, 0.65–1.5 \(\mu\)S (\(G_{max}/G_{min} = 2\)), an improvement in comparison to the \(\approx 250\) s retention time reported for PEDOT:PSS.
synapses programmed within a similar $G_{\text{max}}/G_{\text{min}}$ range under inert environment.\cite{19} Previously studied PEDOT:PSS channels contained polyethyleneimine (PEI), which is an important additive to improve state retention. However, PEI also plays a role in destabilizing the states that are more conductive than the equilibrium state, acting as an electron donor to annihilate electrochemically generated holes until the conductivity decays to its initial state.\cite{19,20} When a PEDOT:PSS/PEI device is charged to a lower conductivity, the PEI additive diffuses out of the channel and into the electrolyte, causing conductivity to increase over time toward the initial state.\cite{19,20} Yet, the conductance of RuPBA, when programmed at the lower range ($G < G_0$), does not trend back toward $G_0$ because RuPBA does not rely on a redox buffer such as PEI. This implies that, with only mild loss of analog range, non-volatile programming in the range of 0.65–1.5 $\mu$S can still enable efficient in situ learning and retention for embedded biocompatible applications, with only minor alterations to normal training needed (e.g., an array calibration step after each epoch to detect outlier weights exceeding some threshold above $G_0$, where they can be clipped/RESET). As most neural network weights are low significance (low-conductance), the hardware mapping for this scheme is natural and could lead to low overall error profiles at inference stage.\cite{22} Meanwhile, the range clipping would not be a major detriment to learning performance, since a compressed range of 6–8 bits writable space is more than sufficient for most online learning applications using emerging non-volatile memory devices\cite{23} even when considering write noise in the loop.\cite{24}

**Endurance**: The channel conductance can be repeatedly cycled using $10^6$ switching pulses without altering switching characteristics (Section S5, Supporting Information).

---

**Figure 1.** Reversible electrochemical doping of RuPBA. a) Idealized vacancy-free structure of partially lithiated RuPBA, $\text{Li}_3\text{Ru}_2[\text{Ru(CN)}_6]_2$, showing proposed cross-pore (CP) and nearest neighbor (NN) charge transfer paths. b) Schematic representing reversible $\text{Li}^+$ ion insertion into the RuPBA film at the gate and channel separated by a $\text{Li}^+$-containing ionogel electrolyte (see Section S3, Supporting Information, for a detailed description of the ECRAM device architecture). c) Transfer curve for a RuPBA/Li-ionogel ECRAM device showing the resulting source-drain current of the channel ($i_{sd}$) on a linear scale (left $y$-axis, blue) and channel conductance on a logarithmic scale ($G$, right $y$-axis, red) when scanning the gate-drain voltage ($V_{gd}$) at 30 $\mu$V s$^{-1}$ and applying a source-drain bias of 0.1 V. The dashed box designates the region where $i_{sd}$ increases linearly as a function of electrochemical charge. Channel length ($L = 100 \mu$m), width ($W = 3000 \mu$m). Measurement performed under ambient air. d) Scheme conveying the change in Ru valency and degree of lithiation as the channel undergoes oxidation (Ox) and reduction (Re). Numeric labels on Ru atoms represent formal oxidation states and valence mixing. The region shown in pink highlights the proposed CP mixed valence conduction pathway, where electron delocalization occurs between neighboring N-coordinated Ru centers while C-coordinated Ru centers maintain localized 2$^+$ formal oxidation states.
Figure 2. Li-RuPBA ECRAM device performance. a) Nonvolatile channel conductance switching during pulsed programming at $V_{gd} = +1/-1$ V for depression/potentiation at 0.75 ms gate pulse duration. b) Long-term retention of five programmed conductance states in a single ECRAM device. c) Simulated performance for neuromorphic tasks. Error bands represent standard deviation. d) Pulsed conductance programming with different channel dimensions, as labeled. “Write Time” represents the total time that voltage is applied to the gate, summed from multiple $+/-1$ V write pulses. Log-log plots showing relationship of channel area, $A$, to e) switching times, $\Delta t_{\text{min}}$, and f) switching energies, $\Delta E_{\text{min}}$, required to change the channel conductance by an average value of $\pm1.0$ nS. Inset tables show values obtained by extrapolation of the linear fits (red lines). The durations of the applied write pulses were 0.75, 6, and 10 ms in order of increasing area; this was done to achieve roughly equal numbers of conductance states per ramp, $\approx 70$ states for each of the three devices. The channel $L$:W aspect ratio of devices for parts (d–f) is 1:7.5, keeping the RuPBA film thickness constant at $\approx 0.6$ µm. Error bars represent the standard deviations for parts (e,f). See Table S3, Supporting Information for number of switching pulses analyzed per device. All measurements were performed under N$_2$ atmosphere at $T = 300$ K.
**Simulation of RuPBA Neural Network Training:** From this data, we evaluate online learning by simulating a hardware multi-layer perceptron populated with RuPBA synapses. Due to the existence of a smooth, linear workable region optimal for on-chip backpropagation,[23] the RuPBA synapse generally performs excellently in the context of online learning. As shown in Figure 2c, on smaller tasks, such as the Iris flower classification problem[26] and the optical character recognition task,[27] RuPBA synapses achieve close agreement with ideal synapses (numerical). On larger neuromorphic tasks such as the fashion-MNIST[28] and MNIST task,[29] the gap between ideal and RuPBA devices diverges slightly more. Overall, our results are comparable to those of other leading linear and symmetric nonvolatile memory candidates (Section S6, Supporting Information).[13a,b,14b,30]

**Efficiency and Scaling Relationship:** The programming speed and energy efficiency of an ECRAM synapse depend on the electrochemical current of the “write” step when a gate voltage is applied to change the redox state of the channel. Write currents should be minimized to reduce the energy cost. However, higher faradaic write current densities should increase the ECRAM switching rate (faster charging). Figure 2d shows conductance versus write time traces for three devices with different channel areas, A, but a similar length/width aspect ratio (L/W = 1:7.5). The smallest device clearly operates more quickly, completing 12 potentiation/depression cycles before the larger device can finish the first cycle. The average times and energies required to switch the conductance by a magnitude of 1 nS are plotted versus channel area in Figure 5e,f (see Section S7, Supporting Information, for analysis details). The smallest device achieves a switching time of 0.75 ms, comparable to the duration of action potentials in biological neurons.[33] The relationships are highly linear with log-log slopes of 1. From extrapolation, we predict that RuPBA ECRAM devices of similar architecture with 100 nm channel length should switch on the timescale of ~1 ns, much faster than biosynapses, with ≈1 fJ write energy, a lower energy cost compared to ≈10 fJ per synaptic event in biological synapses.[11] We anticipate that RuPBA devices fabricated with thinly layered channel/electrolyte/gate vertical architecture[13c] would significantly lower the electrolytic gating resistance and increase the overall switching efficiency.[14d]

**Neuromorphic Aspects:** In analogy to neurological processes, the programming pulses applied to the gate simulate inputs (e.g., action potentials and neurotransmitter release) from a virtual presynaptic neuron. The ECRAM channel essentially mimics the function of the postsynaptic density at the dendrite attached to a postsynaptic neuron. The resulting changes in chemical composition (Li content) in the ECRAM channel/gate cause the strength of the synapse to change, that is, the electronic structure of RuPBA and therefore the channel resistivity. Thus, the nonvolatile conductance switching discussed in this section demonstrates long-term synaptic plasticity.

### 2.2.2. Short-Term Synaptic Plasticity and Spike Time Dependence

Gate pulses of shorter duration and/or lower voltage cause a volatile change in the channel conductance, demonstrating short-term plasticity (Section S8, Supporting Information). We found that a gate voltage of ~0.1 V at durations less than ~100 ms generally gives rise to short-term potentiation. The plasticity not only depends on the duration/voltage of the programming pulse, but also the delay time between the applied pulses. A double-exponential fit of the paired-pulse facilitation (PPF) index as a function of delay time between pulses of equal duration suggests at least two relaxation processes with time constants, $\tau_1 = 1.7$ ms and $\tau_2 = 12$ ms for pulse durations of 1 ms and $\tau_1 = 6$ ms and $\tau_2 = 50$ ms for pulse durations of 10 ms, similar in timescale to temporal signaling processes in biological networks (Figure S8, Supporting Information).

### 2.3. Potential for Biosensing and Brain-Computer Interfacing

#### 2.3.1. DA-Mediated Plasticity via ECRAM Configuration

RuPBA undergoes reduction upon reaction with DA, an important neurotransmitter, thus inserting cations from the electrolyte to RuPBA (Figure 3c). Figure 3a shows the design for a modified ECRAM device that allows DA to react with the RuPBA gate while preventing the DA from directly interacting with the RuPBA channel (see figure caption for details). DA would need to travel laterally through more than 1 mm of hydrophobic ionogel to reach the channel, and we did not observe any evidence of the aqueous DA buffer solution leaking through the adhered plastic well. Thus, the aqueous buffer electrolyte (and DA medium) forms a stable interface with the Li ionogel electrolyte that bridges a portion of the gate to the full channel. The remaining region of the RuPBA gate serves as the site for DA/RuPBA redox at the solution/RuPBA interface.

When a depressing/potentiating double-pulse is applied in the absence of DA in the buffer solution, the channel conductance decreases and then increases back to the initial state (Figure 3d, 0–500 s, first 3 sets of voltage double-pulses). Upon introduction of the first aliquot of DA solution, the channel conductance remains unaltered because the gate is at open circuit. However, upon application of the same pair of pulses, the conductance decreases and reaches a steady state. Figure 3d shows that the device conductance decreases by AG when incrementally increasing the DA concentration, leading to the dose-response calibration curve. (See Section S9, Supporting Information, for a more detailed description of the device operation). The RuPBA synapse achieves the detection of DA at 4 µm concentration, comparable to PEDOT:PSS-based devices.[15,32] However, distinct from OECT-based anlyte sensing, the RuPBA ECRAM device undergoes a nonvolatile change in conductance state, demonstrating DA-triggered long-term synaptic plasticity, similar in essential function to the bio/artificial hybrid synapse proposed by Keene et al.[15]

#### 2.3.2. DA Chemristor via Two-Terminal Configuration

A simple two-terminal RuPBA resistor also functions as a DA sensor because the redox reaction causes the conductivity of RuPBA to decrease (Figure S10, Supporting Information). However, in contrast to the DA-mediated ECRAM synapse described above, a two-terminal RuPBA chemristor cannot transduce DA...
activity to nonvolatile memory because the device conductance continues to decrease over time if the RuPBA channel remains in direct contact with the DA-containing solution.

2.3.3. Biocompatibility of RuPBA

For successful bio-interfacing, neuronal cells should be able to grow and thrive on RuPBA films. We find that cells seeded onto RuPBA films divide at a rate comparable to control cells, and that their viability is as high as control cells (Section S10, Supporting Information). Optical and scanning electron micrographs of the cells show interaction with and adherence to the RuPBA substrate. We conclude that RuPBA is nontoxic and non-refractory to cell growth. The compatibility of RuPBA with live neuronal cells signifies a promising first step toward utilizing ECRAM to integrate biological and artificial neural networks.

2.3.4. Challenges for Potential Brain-Computer Interface

The next goal is to switch the ECRAM synapse via DA released by dopaminergic neuronal cells, as was demonstrated for a PEDOT:PSS-based device. However, the RuPBA ECRAM device conductance also switches after reacting with glucose, which should be kept at very high concentrations to keep the cells alive. Thus, a major technical challenge going forward is to enable higher specificity for DA by preventing reaction with glucose and other electroactive species in the cell culture media. We also predict similar problems for PEDOT:PSS-based devices because the high-conductivity formulation (PH 1000), as used by Keene et al., is known to react with species in commonly used cell culture media.

2.4. Spectroscopic Probing of Electrochemically Tunable RuPBA Electronic Structure

In situ UV/Vis/NIR spectroscopy provides a means to probe the electronic structure of RuPBA during electrochemical cycling. The visible color change of an electrochronic RuPBA film on FTO/glass is shown in Video S1, Supporting Information. The film changes color from beige at the more reduced state to blue grey at the more oxidized state. Figure 4a shows the evolution of absorption spectra as a RuPBA/ITO electrode is scanned from a fr state at −0.2 V to a partially oxidized state at 1.0 V (versus

Figure 3. Dopamine (DA) sensing with modified ECRAM cell. a) Sketch of modified device for dopamine sensing. The Li ionogel fully covers the RuPBA channel and bridges the lateral gap between channel and gate, but only partially covers a region of RuPBA gate (roughly 40%). The aqueous DA-free or DA-containing buffer solution contacts the remaining portion of the RuPBA gate, along with a small region of the ionogel-covered portion. The distance of water/ionogel interface parallel to the substrate plane (not shown in sketch) is roughly between 0.1 and 0.5 mm. Channel dimensions: \( L = 100 \mu m \); \( W = 3000 \mu m \). b) Illustration of dopamine release from vesicles of a presynaptic neuron (top) to receptors of a postsynaptic neuron (bottom). c) Schematic of dopamine reaction with RuPBA in the portion of the device gate enclosed by the well. d) Conductance trace during incremental additions of dopamine and inset showing corresponding dose-response plot. In the inset of part (d), \( \Delta G = G_0 - G \), where \( G_0 (=4.85 \mu S) \) is indicated by the topmost dashed horizontal red line on the conductance trace. The red “\( \Delta G \)” label shows the change in conductance that results from the first addition to giving \([DA] = 4 \mu m \). See Section S8, Supporting Information, for a more detailed description of device operation.
ments of the conductance and IVCT absorbance in the channel region of an ECRAM device after potentiostatic charging at varied gate voltages (Vg).

Following Behera et al., we assign the bands in RuPBA to first, a MLCT band and IVCT reaction, respectively. As the film is oxidized, the MLCT intensity decreases while the IVCT intensity increases. Like the conductance versus gate voltage trend of Figure 1c, the relationship of IVCT absorbance to electrode potential in Figure 4b is sigmoidal and reversible. The absorbance versus potential response is consistent over multiple cycles in this ΔE = 1.2 V potential window. Figure 4c shows the interrelationship of applied gate voltage, IVCT absorbance, and conductance when switching conductance across four orders of magnitude in a RuPBA ECRAM device. The correlation of conductance to IVCT absorbance signifies that the electronic conductivity of RuPBA is inextricably linked to the rate of IVCT.

When extending the applied potential of the RuPBA/ITO electrode to 1.4 V versus Ag/AgCl, we observe an additional trend in the IVCT region of the UV/Vis/NIR spectra (Section S11, Supporting Information). The lowest energy maximum at ~6450 cm⁻¹ follows the trend as discussed above from ~0.2 to 1.0 V, but then decreases in absorbance from 1.0 to 1.4 V. The absorbance at ~13 000 cm⁻¹, however, continues to increase as RuPBA undergoes oxidation to 1.4 V. The two observed trends reveal that two distinct IVCT processes occur in RuPBA, and that the absorbance of the lower energy IVCT correlates with conductivity.

Voltammetric cycling of RuPBA within this larger electrochemical window causes hysteresis in absorbance between the forward/reverse scans and a decreasing overall absorbance with increasing cycle number, suggesting that overoxidation of RuPBA causes irreversible degradation of the material (Figure S12b, Supporting Information). The absorbance-potential trend correlates to the observed hysteresis and decreasing conductance range for ECRAM device conductance switching during cycling at more extreme gating voltages (Figure S3, Supporting Information). Thus, overoxidation of the RuPBA channel should be avoided during device operation. Excellent ECRAM switching linearity and endurance (Figure 2; Figures S6 and S7, Supporting Information) are achieved by keeping the oxidation state of the RuPBA channel well below the degradation threshold.

2.5. Mechanistic Interpretation

2.5.1. Application of Electron Transfer Theory

The strong correlation of IVCT absorbance with conductivity supports a mechanism whereby electronic transport in RuPBA occurs through adiabatic intramolecular CT reactions. As shown in Figure 5a, deconvolution of the UV/Vis/NIR spectrum for a film of the as-synthesized RuPBA suggests at least seven different overlapping optical absorption bands in the wavenumber (ν) range of 35 000 to 4000 cm⁻¹, consistent with the previous report. We assign the two lowest energy bands at ~8400 cm⁻¹ (1.0 eV) and 5100 cm⁻¹ (0.6 eV) to two different IVCT transitions, as depicted in Figure 5a,b. The higher energy band (IVCTₐ) corresponds to electron transfer from a redox pair of N-coordinated Ru (N-Ru) to its nearest neighbor, C-coordinated Ru (C-Ru), as separated by the cyanide bridge. The lower energy band (IVCTₕ) corresponds to “cross-pore” transfer between two N-coordinated Ru(Ru) redox pairs. Our interpretation of these two separate IVCT bands agrees with that of isolated trinuclear and tetranuclear CN-bridged Ru complexes. Both IVCT bands are best fit using an asymmetric peak shape, which indicates that the as-RuPBA fits in a transition regime of electronic delocalization according to Robin-Day classification, exhibiting properties typical for both class 2 (semiconductor) and class 3 (metallic) systems, or the so-called “class 2B” system. In contrast, PB belongs to the class 2A regime involving more localized charges.

The effective donor-acceptor coupling, HEff, and activation energy, Eₐ*, were determined based on the IVCTₕ peak energy and shape following an equivalent two-state model for the three-state system depicted in Figure 5b (see...
Figure 5. Interpretation of optical charge transfer bands from UV/Vis/NIR absorption spectrum of RuPBA. a) Reduced absorption spectrum and fitted asymmetric Gaussian peaks, highlighting two different IVCT bands for transfer between nearest neighbor cyanide bridged Ru centers (IVCT_{NN}) and cross-pore between N-coordinated Ru centers (IVCT_{CP}), as depicted in the inset scheme. The absorbance is divided by ν to accurately determine the reorganization energy and coupling in accordance with theory.[9b] b) Schematic representation for potential energy surface diagram of IVCT based on a three-state model. Red dashed lines labeled A, B, and C convey three parabolic overlapping diabatic energy surfaces, where the energy minima for A, B are equivalent and occur at X=0.1. The higher energy minimum for C occurs at X=0.3. Blue lines labeled 1, 2, and 3 represent the adiabatic states resulting from electronic coupling between N-coordinated donors, acceptors, and hexacyanoruthenate bridge states. The IVCT_{CP} product and reactant states are of equivalent ground state energy due to symmetry. The third possible state (state 3), formed from IVCT_{NN}, is thermodynamically disfavored. E_{nn} and E_{cp} represent hv for the deconvoluted peak maxima of IVCT_{NN} and IVCT_{CP}, respectively.

Section S12, Supporting Information). The fit of the IVCT_{CP} band for as-RuPBA gives E_{cp}^* = \lambda = 0.64 eV and a large coupling, $H_{eff} = 0.22$ eV; this leads to $E_{nn}^* = 16$ meV, which is less than $k_BT$ at room temperature. The IVCT_{CP} rate constant is then

$$k_{ct} = \kappa \nu_e \exp\left[-E_{nn}^*/(k_BT)\right]$$

(1)

where $\kappa$ is the probability of electron transfer at the configuration coordinates ($X$) when the activation barrier is minimized and $\nu_e$ is a nuclear vibration frequency,[9b] here assigned as the cyanide bridging ligand vibration (~2130 cm$^{-1}$) shown in the Raman spectra of RuPBA (Section S13, Supporting Information), giving $\nu_e = 6.4 \times 10^{13}$ s$^{-1}$. The calculated electronic frequency[9b,36] ($\nu_{el} = 1.0 \times 10^{15}$ s$^{-1}$, see Section S12, Supporting Information) is much higher than $\nu_e$, such that $\kappa$ is essentially unity, as expected. This leads to a very fast rate constant of $k_{ct} = 3 \times 10^{13}$ s$^{-1}$, only slightly lower than $\nu_e$, further supporting a Robin-Day class 2B assignment for as-RuPBA, but very close to class 3 delocalization.[9b] The $k_{ct}$ value corresponds to an IVCT timescale of 30 fs, which is within the sub-picosecond range measured for CT in PBAs by time-resolved spectroscopy.[37]

Rosseinsky and coworkers presented a simple expression for IVCT-based conductivity of PB following the treatments described by Austin-Mott and Robin-Day.[35,36] We propose a similar relationship below.

$$\sigma = p e^2 d^2 k_{ct} / (2k_BT) = c p \mu_i$$

(2)

Here, the conductivity ($\sigma$) depends on the number density of hole charge carriers ($p$) and the distance between reactant centers ($d$). For IVCT_{CP}, the shortest distance between N-Ru centers is $d \approx 7.4$ Å based on the XRD pattern of RuPBA (Section S14, Supporting Information). Equation (2) also shows how $k_{ct}$ and $d$ relate to the hole mobility; $\mu_h = ed^2 k_{ct} / (2k_BT)$. For as-RuPBA, $\mu_h \approx 4$ cm$^2$ V$^{-1}$ s$^{-1}$, which is comparable to that reported for PEDOT:PSS.[39] Because both IVCT_{CP} absorbance and conductivity increase as the RuPBA partially oxidizes, we propose that $p$ must relate to the concentration of mixed valence N-Ru sites, as depicted in Figure 5. The maximum carrier concentration occurs when the valence mixing is 1:1 II:III between N-Ru centers, corresponding to a net mixing of 3:1 II:III for all Ru centers (or fractional valency equivalent of 2.25), assuming an ideal defect-free lattice. By application of these IVCT assignments to the relationship in Figure 4b and consideration of the measured steady-state open circuit voltage of the initial state before cycling (0.3 V versus Ag/AgCl), we infer that the fractional valency of as-RuPBA is =2.1; this is consistent with the high potassium content (K:Ru = 1:2.6 atom ratio) measured by elemental analysis and the low Ru 3p and 3d binding energies measured by X-ray photoelectron spectroscopy (see Experimental Section and Section S15, Supporting Information).

Closer analysis of the spectra in Figure 4a reveals that the IVCT band manifold not only increases in absorbance, but also shifts by more than 0.3 eV to lower energy throughout the course of oxidation from fr-RuPBA to the most conductive partially reduced (pr) mixed valence state at 1.0 V, signifying that $\lambda$ and $E_{nn}^*$ decrease while $k_{ct}$ and $\mu_h$ increase (see Section S12, Supporting Information). Spectroscopically determined parameters at varied $E$ indicate that mobility increases from 1 to 4 cm$^2$ V$^{-1}$ s$^{-1}$ when oxidizing RuPBA over a small
potential range from $E = 0$ to $0.1$ V (Table S4, Supporting Information). However, the mobility does not vary significantly at potentials between $0.1$ V and the most conductive state ($E = 1.0$ V), implying that the increasing carrier concentration from oxidation is the sole contributor to conductance switching in the $V_E$ range roughly between 0 and $-0.5$ V (Figure 1c). The trend of increasing, constant, then decreasing mobility during partial oxidation of fr-RuPBA agrees well with the interpretation of the transfer curve above (Figure 1c and Figure S2 of the Supporting Information).

2.5.2. Application of DFT

The partial density of states (pDOS) computed by DFT for different oxidation/lithiation states of RuPBA are shown in Figure 6. The “fully reduced,” “partially reduced,” and “neutral” forms correspond to compositions of $\text{Li}_x\text{Ru}_3[\text{Ru}(\text{CN})_6]_2$, where $x = 4$, 3, and 2, respectively. The pr form (pr-RuPBA), as depicted in Figure 1a, is predicted to have a direct band gap of 0.50 eV, in agreement with the experimentally determined IVCTCP maximum (0.55 eV) for the most conductive state (Table S4, Supporting Information). Such agreement between computed band gap and measured IVCT excitation energy was also reported for PB.\(^{[40]}\) The fr form is predicted to have a large band gap (4 eV), comparable to the energy of the observed MLCT band ($h\nu_{\text{max}} = 4$ eV). The calculated hole effective masses ($m_h$) for RuPBA range from 0.4 to 0.7 (see Table S5, Supporting Information); these values are similar to known semiconductors such as p-type germanium.\(^{[41]}\) The smallest $m_h$ value corresponds to the pr-RuPBA state. Based on scattering theory (see “DFT Computation” for details), we predict a hole charge mobility for pr-RuPBA of 5 cm$^2$ V$^{-1}$ s$^{-1}$, which is in remarkable agreement with our experimental estimate from the MHT analysis above (4 cm$^2$ V$^{-1}$ s$^{-1}$). The pDOS for pr-RuPBA reveals a delocalized electronic structure, but valence and conduction band states closest to the Fermi energy remain primarily associated with N-Ru sites. This suggests that the lowest energy excitation is between N-Ru sites, which agrees with our interpretation of the IVCT spectra (Figure S5). Thus, both band and electron transfer theories support a mechanism whereby the electrochemically tunable degree of mixed valency between N-Ru centers directly relates to charge carrier concentration.

We also compute pDOS and $m_h$ values for PB at different redox states for comparison (Section S16, Supporting Information). The $m_h$ values for PB (Table S6, Supporting Information) are larger than those of RuPBA (Table S5, Supporting Information), ranging from 1.3 to 2.9, in agreement with previously published values\(^{[42]}\) which is consistent with the predicted flat bands and localized states (Figure S19, Supporting Information), and in agreement with measurements by Long that showed RuPBA is substantially more conductive than PB.\(^{[43]}\) The differences between PB and RuPBA band structures primarily arise from their different electron spin configurations (Figure S20, Supporting Information). Unlike the high/low spin configuration of PB,\(^{[44]}\) both N-coordinated and C-coordinated metal atoms of RuPBA are low spin, allowing for better energy alignment between neighboring Ru atoms and a more delocalized electronic structure (Figure S21, Supporting Information). The delocalization, in the NN direction (Figure S22, Supporting Information), contributes to lower $m_h$ in RuPBA compared to PB.

2.6. Effect of Grain Boundaries

The estimated mobilities presented above specifically refer to electron-hole transport within the bulk CN-bridged framework. Assuming a hole density ($p$) of $\approx 10^{21}$ cm$^{-3}$, we estimate a bulk crystal conductivity greater than 100 S cm$^{-1}$ for the most conductive state (pr-RuPBA), which is $\approx 10$ 000 times greater than the measured maximum conductivity. The inkjet-printed films, however, are composed of RuPBA nanocrystals. (Figure S16, Supporting Information). Measurements of DC conductivity as a function of temperature for as-RuPBA give an activation energy of 0.18 eV (Figure S1, Supporting Information), which is roughly ten times higher than the activation energies estimated above from spectroscopy (Table S4, Supporting Information). CT across grain boundaries likely plays a limiting role in the observed film conductivity\(^{[45]}\) in addition to the contact resistance at the RuPBA/Au interface. Importantly, this activation energy is roughly $\frac{1}{4}$ of the measured reorganization energy for the IVCTCP band ($\lambda = 0.64$ eV), consistent with very weak coupling and polaron hopping\(^{[46]}\) between charge-localized N-Ru centers at the interfaces between neighboring nanocrystals. We propose that electronic coupling is much weaker across grain.

Figure 6. DFT/HSE06 band structures and density of states of RuPBA in the neutral, partially reduced, and fully reduced states. The hole effective masses are reported in Table S5, Supporting Information.
boundaries due to the absence of NCRuCN bridges between N-coordinated Ru centers.

3. Conclusion

We have shown that the choice of candidate active materials for ECRAM and electrochemical transistors is not strictly limited to conductive organic polymers and transition metal chalcogenides, but also includes coordination frameworks like RuPBA. Our findings open a window to study electrochemically tunable conductivity in related mixed valence coordination structures such as other PBAs, coordination polymers, and metal-organic frameworks. Two different theoretical approaches, electron transfer theory, and Boltzmann transport theory, independently predict similar carrier mobilities within the RuPBA bulk. The IVCT spectroscopic analysis emphasizes that the Marcus-Hush model is not only applicable to CT kinetics in small molecules, but also provides physical insight into mixed valence conductors that belong to the Robin-Day class 2–3 transition regime,[9d,35] exhibiting characteristics of both intervalence hopping and band-like carrier transport due to an intermediate degree of electron delocalization. Both theoretical treatments also support the proposed IVCT transport pathway. We anticipate major improvements to ECRAM and other electronic applications as devices are made smaller and look forward to taking advantage of RuPBA’s sensitivity to DA to achieve communication between biological and artificial neural networks.

4. Experimental Section

All reagents and solvents were purchased from Sigma Aldrich unless otherwise noted. All water was filtered and deionized to 18.2 MΩ. All reagents and solvents were purchased from Sigma Aldrich unless otherwise noted. All water was filtered and deionized to 18.2 MΩ.

Preparation of Li Ionogel Ink: Lithium bis(fluorosulfonyl)imide, LiFSI, (2.035 g) was dissolved in 10 mL of 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pry14TFSI) ionic liquid by stirring overnight in an Ar-filled glovebox to give a 1.0 m LiFSI in Pry14TFSI solution. Preparations of the sol-gel precursor for the ionogel ink were based on the method described by Dunn and coworkers.[31] A 300 µL volume of tetracyclohexylsilicate (TEOS) was added to 300 µL of triethoxysilane (TEVS) and sonicated for 15 min. While under sonication, 300 µL of formic acid was added to the TEOS/TEVS mixture and allowed to sonicate for 15 min to give the sol-gel precursor. A 550 µL aliquot of the sol-gel precursor was then added to 450 µL of the ionic liquid (1.0 m LiFSI in Pry14TFSI) and sonicated 15 min to give a clear solution, which was subsequently diluted with 1 mL ethanol for use as the Li ionogel ink.

Preparation of Protic Ionogel Ink: A solution containing 17.6 wt% protic ionic liquid (diethylmethylammonium trifluoromethanesulfonate, DEMATFO, 98%, IOLITEC), 4.4 wt% poly(vinylene fluoride-co-hexafluoropropylene), and 78 wt% dimethylacetamide (DMA) was prepared by sonication and subsequently diluted by a factor of 4 with additional DMA solvent.

ECRAM Device Fabrication: Gold patterns for ECRAM devices and Van der Pauw samples were fabricated on nanosilica-coated polyethylene terephthalate (PET) printing media (Novele, Novacentrix) via e-beam evaporation using custom-designed shadow masks (Stencils Unlimited) by depositing 5 nm Ti adhesion layer, followed by 150 nm Au top layer. RuPBA and ionogel layers were printed over the Au-patterned PET substrates using a Dimatix Materials Printer (DMP-2850) with DMC-T1610 ink cartridges. Removable Scotch tape was used to adhere the back side of the PET substrate to an SiO2-coated Si wafer. The fiducial camera of the DMP was used to guide alignment of the RuPBA prints to the Au electrode pattern array.

RuPBA films for ECRAM devices were printed using a carbon temperature of 29 °C and substrate temperature of 55 °C. Device channels were printed with one jet nozzle at 20 µm drop spacing for optimal film quality and feature resolution, with a total of 10 print cycles. Channel films included ~75 µm of overlap with the Au contacts. For the device gates, 15 RuPBA print cycles were performed using 11 nozzles at a drop spacing of 31 µm. 2-min rest periods were inserted in between prints for each device row to keep the cartridge temperature from exceeding 32 °C, which was found to help prevent nozzle clogging. For these devices, RuPBA was printed over the entire area of Au gate electrode and the channel region, similar to the other ECRAM devices. The ionogel was printed over the region shown in Figure 3a, leaving a 4 by 4 mm RuPBA/Au region without ionogel coating. An acrylic adhesive backed plastic well was fabricated by laser cutting and attached to the device. The well was initially filled with 25 µL of 0.1 m sodium phosphate buffer, pH 5.5. A pipet was used to incrementally add 1 µL aliquots of the DA solution (0.1 mM DA hydrochloride, 0.1 mM sodium phosphate buffer, pH 5.5) to the reservoir.

Film Thickness Measurement: Inkjet-printed films for ECRAM devices and sheet resistance samples were characterized using a 3D optical profilometer (Profilm3D, Filmetrics). 3D image profiles are provided in Section S17, Supporting Information.

X-Ray Diffraction: Powder X-ray diffraction measurements were performed on a PANalytical Empyrean diffractometer equipped with a PIXcel3D detector and operated at 44 kV and 40 mA using Cu Kα radiation (λ = 1.5406 Å). A reflection-transmission spinner was used as a sample holder and the spinning rate was set at 4 rpm. The patterns were collected in the 2θ range of 5 to 75°, and the step size was 0.026°.

X-Ray Photoelectron Spectroscopy: Samples for X-ray photoelectron spectroscopy were prepared by dropcasting the RuPBA ink on an Au-coated SiO2/Si substrate. The spectra were acquired using Al Kα: 1486.6 eV source and monochromator (Scienta Omicron, Inc., XM 1000MkII) under ultrahigh vacuum.
RuPBA Film Conductivity Measurements: Electrical measurements of Van der Pauw samples and pulsed conductance tuning of ECRAM devices were performed under N$_2$ atmosphere at slightly reduced pressure (~600 torr) and controlled temperature using a CPX-VF probe station and temperature controller (Lakeshore). Sheet resistance measurements were performed with a Keysight B1500A semiconductor device analyzer to obtain conductivity based on the measured film thickness. Current–voltage recordings were also performed at each temperature to make sure the response remained ohmic.

**ECRAM Pulsed-Programming Measurements**: Pulsed long-term potentiation/depression programming, paired pulse facilitation, and state retention testing of ECRAM devices were performed using a custom LabVIEW waveform generation program, as previously described,[46,48,51] to control analog voltage outputs and record input current to an NI-DAQ PCIe-6363 at 10 kHz sampling. To switch the ECRAM device gate to open circuit during the “read” steps for long-term plasticity demonstrations, a CMOS analog switch (MAX327, MAXIM Integrated Products) was implemented and powered by a dual output DC power supply (E3620A, Keysight). For paired pulse facilitation experiments, the CMOS switch was omitted and the gate voltage was switched to 0 V between applications of the facilitation pulses. A low-noise current amplifier (FEMTO, DLPCA-200) was used to measure the current at 10$^{-6}$ volts per amperre gain and 200 Hz low-pass analog filter. The gate charge, $\Delta Q$, resulting from each write pulse was measured by integration of the raw current-time traces using the cumulative trapezoidal numerical integration function in Matlab. Measurements of $A_1$ and $A_2$ from PPF raw current-time data were also performed using a custom Matlab script.

**Cell Culture**: Neuro2a cells were purchased from ATCC (CCL-131) and cultured in high-glucose DMEM (Fisher Scientific #11995073) with 10% Fetal Bovine Serum (FBS) (Seradigm Premium Grade, Avantor) and 1% Penicillin/Streptomycin (Thermo Fisher #15140122). Cells were grown at 37 °C and 5% CO$_2$ and passaged/harvested using Trypsin-EDTA (Fisher Scientific #25300120).

**Growth and Viability Assays**: A 1 mg mL$^{-1}$ aqueous dispersion of RuPBA was spotted onto wells of a 24-well plate (200 μL well$^{-1}$) and allowed to dry at room temperature for 1 h. Cells were seeded at densities of 10 000, 25 000, and 50 000 cells well$^{-1}$ in quadruplicate, and allowed to grow for 3 days, either in the presence or absence of RuPBA. At the end of 3 days, cells were harvested, stained with Trypan Blue (1:1 ratio, incubated for 5 min at room temperature), and counted using a BioRad TC20 Cell Counter. Pictures of the cells on the RuPBA substrate were taken using brightfield imaging with the EVOS M5000 imaging system (at 200× magnification).

**Scanning Electron Microscopy**: Cells were prepared for scanning electron microscopy as previously described.[48] Briefly, cells were plated on Nunc Thermax cover slips (Thermo Fisher #150067) and grown for 3 days in DMEM media with 10% FBS (see above). The cover slips were then fixed in 2.5% glutaraldehyde (Fisher Scientific #02957-1) at room temperature for 30 min, washed 3 × 2 min with phosphate buffer, and post-fixed with 1% osmium tetroxide (Sigma #20816-12-0). After another 2-min wash with rinsing buffer and 2 × 2-min washes with deionized water, the coverslips were dried with anhydrous ethanol. Samples were then dehydrated using a CO$_2$ critical point dryer, sputter coated with ≈1 nm Au, and imaged using an FEI Nova NanoSEM 450 at 5 kV accelerating voltage.

**In Situ UV/Vis/NIR and Raman Spectroscopy**: All spectro-electrochemical measurements were performed using a BioLogic SP-300 bipotentiostat.

**DFT Computation**: All DFT calculations were performed using the Vienna ab initio simulation package (VASP).[47] The geometry and electronic properties were predicted using the hybrid HSE06 exchange-correlation functional within the spin polarization formalism. The plane-wave basis set energy cut-off was set to 500 eV and a 3 × 3 × 2 k-point grid was used during geometry optimization (atomic positions and cell volume). The geometries were optimized until all forces were below 0.02 eV Å$^{-1}$. A single-point calculation was then performed, with a k-point grid of 6 × 6 × 4, to determine the density of states. The band structures and hole effective masses ($m_h$) were determined using AMSET[48] which depends on BoltzTrap[49] for interpolation. Seekpath[50] was used to determine the high symmetry band paths; note, some paths have been omitted in Figure 6 and Figure S19, Supporting Information. Three oxidation states were considered for both PB and RuPBA, fr, pr, and neutral. The different oxidation states were achieved by varying the number of Li atoms (4, 3, and 2 Li atoms respectively; note, PB calculations were performed with K in place of Li). An orthorhombic unit cell was used containing 4 Ru (Figure S18, Supporting Information), which was the smallest system allowing for a pr state to be represented (Figures S18 and S22, Supporting Information).

The hole charge mobility was calculated for pr-RuPBA with the PBsol+U functional using a Hubbard $U_p$ value of 4.0 eV (the resulting band gap was in good agreement with HSE06). The plane-wave basis set energy cut-off was set to 500 eV and a 4 × 4 × 3 k-point grid was used during geometry optimization; the geometry was relaxed until all forces were less 0.0005 eV Å$^{-1}$. The elastic constants, effective phonon frequency, static and high-frequency dielectric constants, and deformation potential were calculated at the same level in theory. A signal-point calculation using a denser k-point mesh, 8 × 8 × 6, was used to obtain the wave function coefficients and for band structure interpolation. These properties/calculations were used to determine acoustic deformation, ionized impurity, and polar optical phonon scattering. The reported hole mobility was calculated for a carrier concentration of 1.8 × 10$^{21}$ cm$^{-3}$ which corresponds to 1 carrier per unit volume. The charge mobility calculation was performed using AMSET.[48]
