SAND2022-14184C

Electrochemically Tunable Mixed Valence Conduction in Ruthenium Hexacyanoruthenate

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

242nd ECS Meeting

October 11th, 2022

Atlanta, GA

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

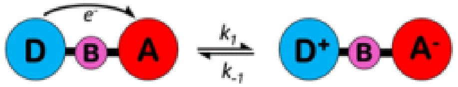
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Intervalence Charge Transfer and Electronic Conduction

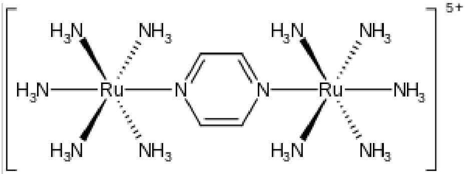
"We may consider mixed valence chemistry as the conceptual link between coordination chemistry and solid state physics." - Andreas Ludi

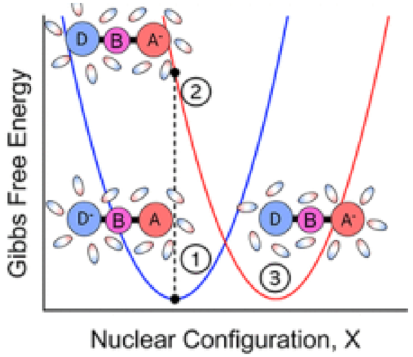
Ludi, A. Descriptive Chemistry of Mixed-Valence Compounds. In *Mixed-Valence Compounds: Theory and Applications in Chemistry, Physics, Geology, and Biology*, Brown, D. B. Ed.; Springer Netherlands, 1980; pp 25-47.

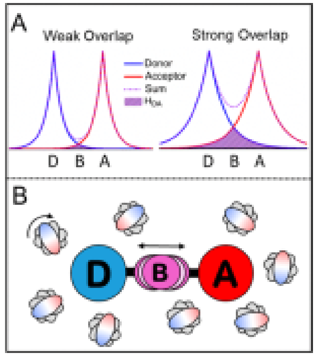
Coordination Chemistry
(Electron Transfer Kinetics, Redox States, Donor-Bridge-Acceptor)

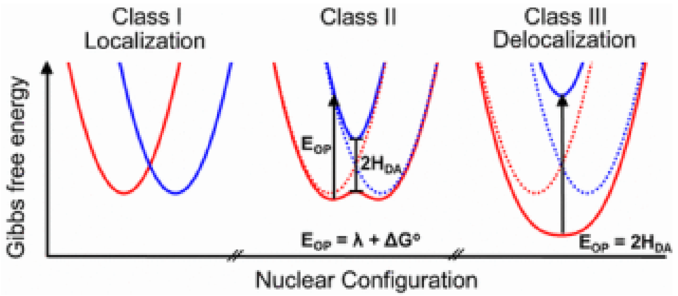


$$k_{ct} = \kappa \nu_n \exp(-E_a^*/k_B T)$$



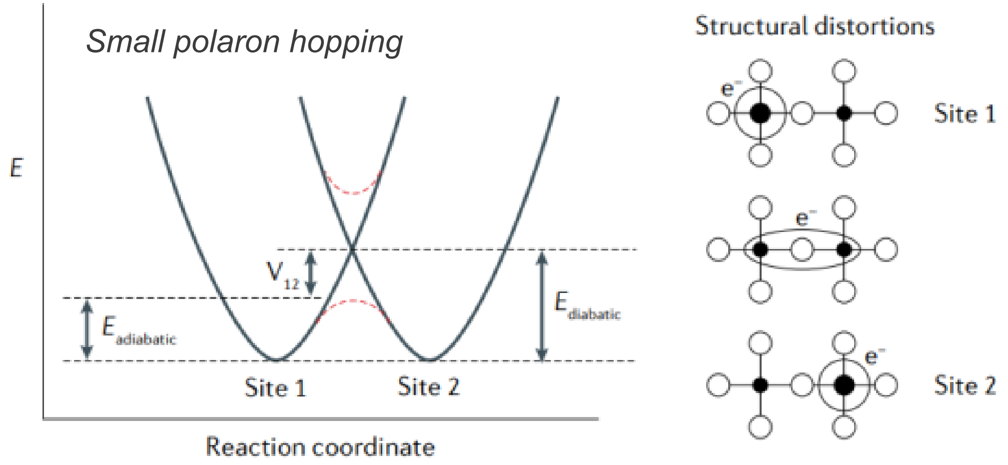


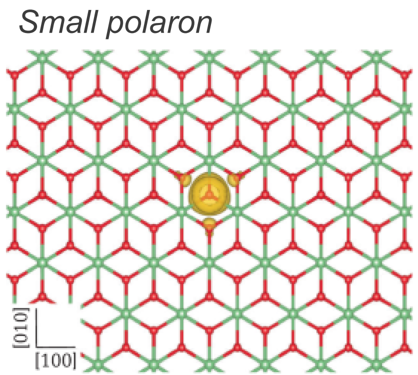


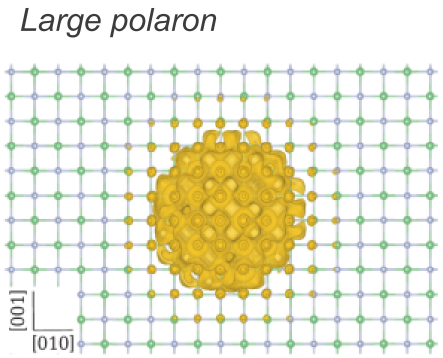


Piechota, E. J.; Meyer, G. J. *J. Chem. Educ.* **2019**, *96*, 2450-2466.

Solid State Physics
(Electron Transport, Quasiparticles)





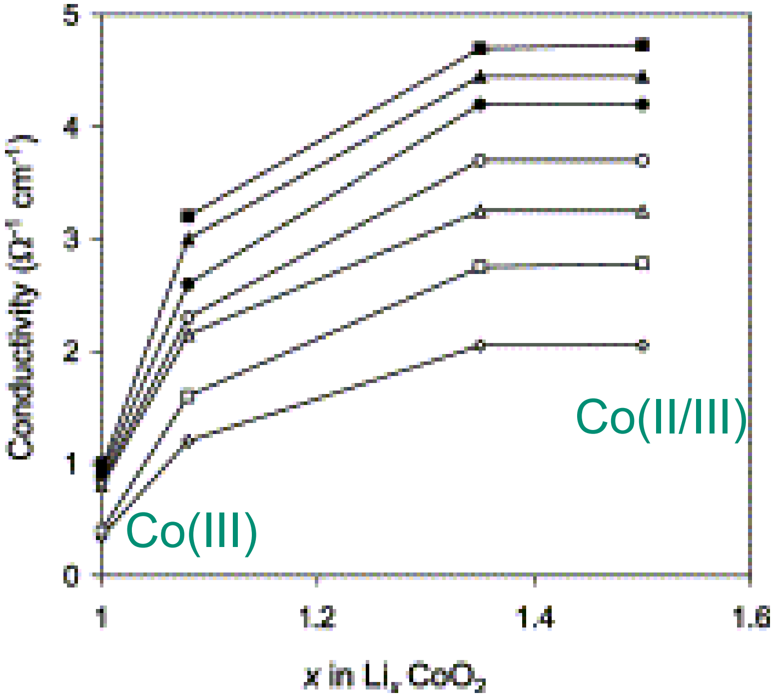


Franchini, C.; Reticcioli, M.; Setvin, M.; Diebold, U. *Nat. Rev. Mater.* **2021**, *6*, 560-586.

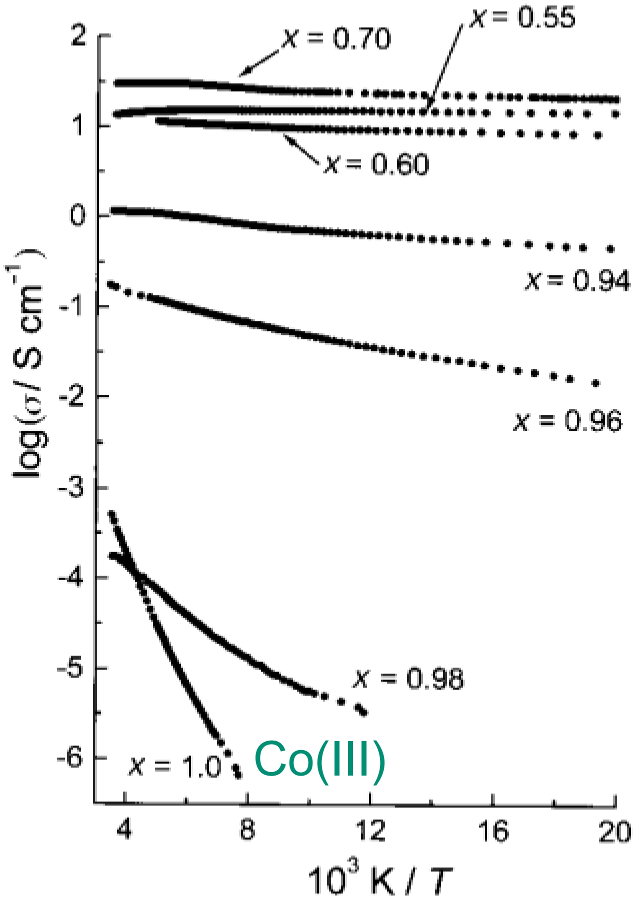
Big Picture Question

What is the relationship between redox state and electronic conductivity in mixed-valence materials?

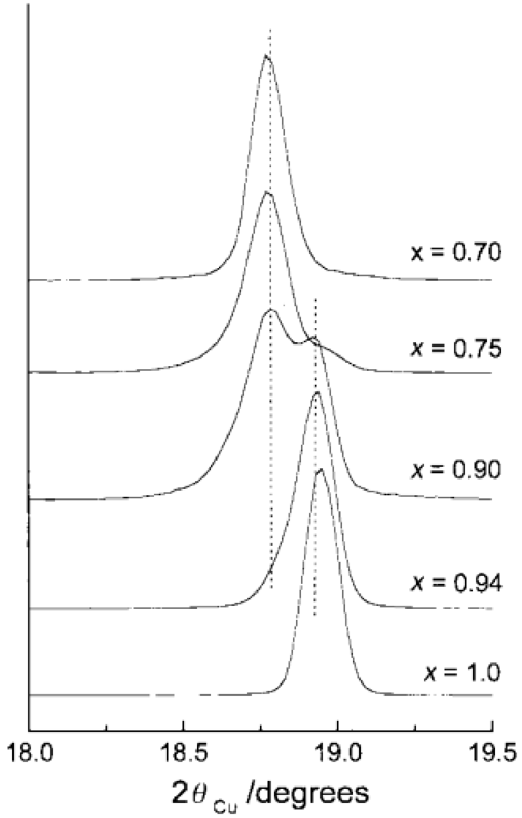
Example: Li_xCoO_2



Co(III/IV)



Phase Transition

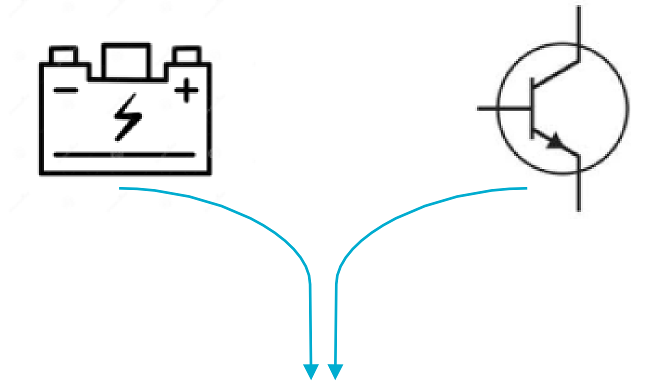


Carewska, M.; S Scaccia, S.; Arumugan, S.; Wang, Y.; Greenbaum, S. *Solid State Ionics*, **1997**, *93*, 227.

Menetrier, M.; Saadoune, I.; Levasseur, S.; Delmas, C. *J. Mater. Chem.* **1999**, *9*, 1135.

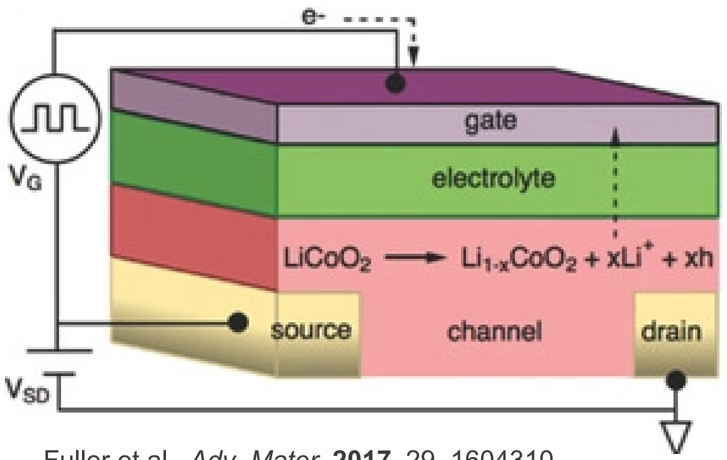
Electrochemical Random Access Memory (ECRAM)

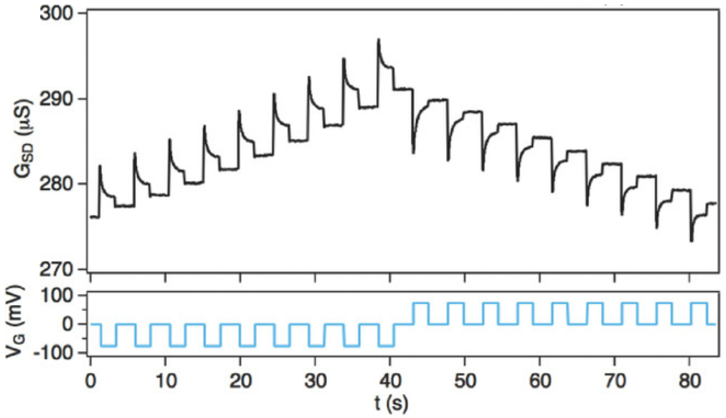
Battery **Transistor**



ECRAM

- ECRAM combines principles of bulk charge storage with electrochemical transistor operation.
- Stored charge → stored conductance.
- Conductance change represents synaptic weight update.





Fuller et al., *Adv. Mater.* **2017**, 29, 1604310.

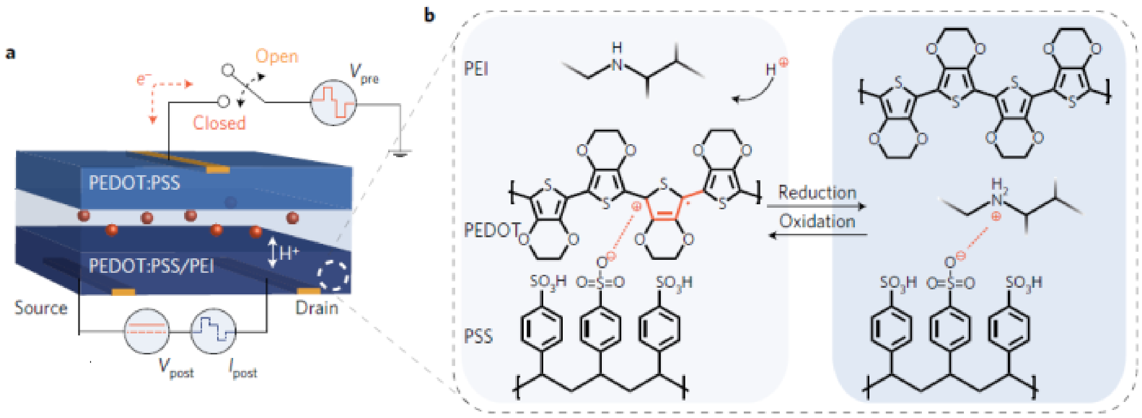
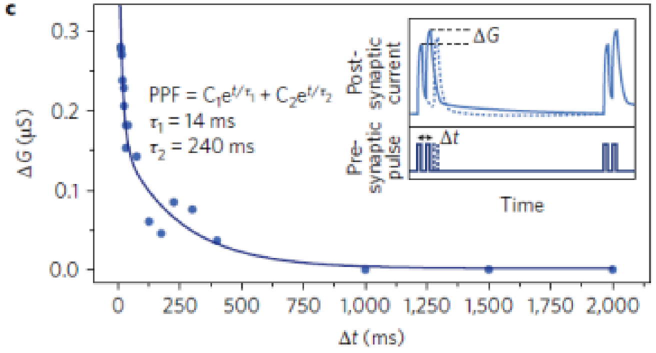
	FET	RRAM	ECRAM
Design	3-terminal, dielectric	2-terminal	3-terminal, electrolyte
Switching mechanism	Field effect	Phase-change, conductive filament	Electrochemical doping (electron transfer, ion insertion)
Changes to channel conductivity	Localized near interface	Localized at phase-change regions	Homogeneous
Timeline: **first functional devices**	1940s	1960s	2017

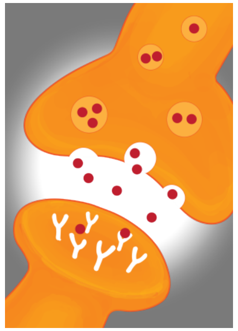
Practical Motivation: Analog Circuits for Neuromorphic Computing

Problem: Conventional hardware for driving neural network computations (CMOS integrated circuits) are inefficient.

Solution: New concepts for all-analog computation.

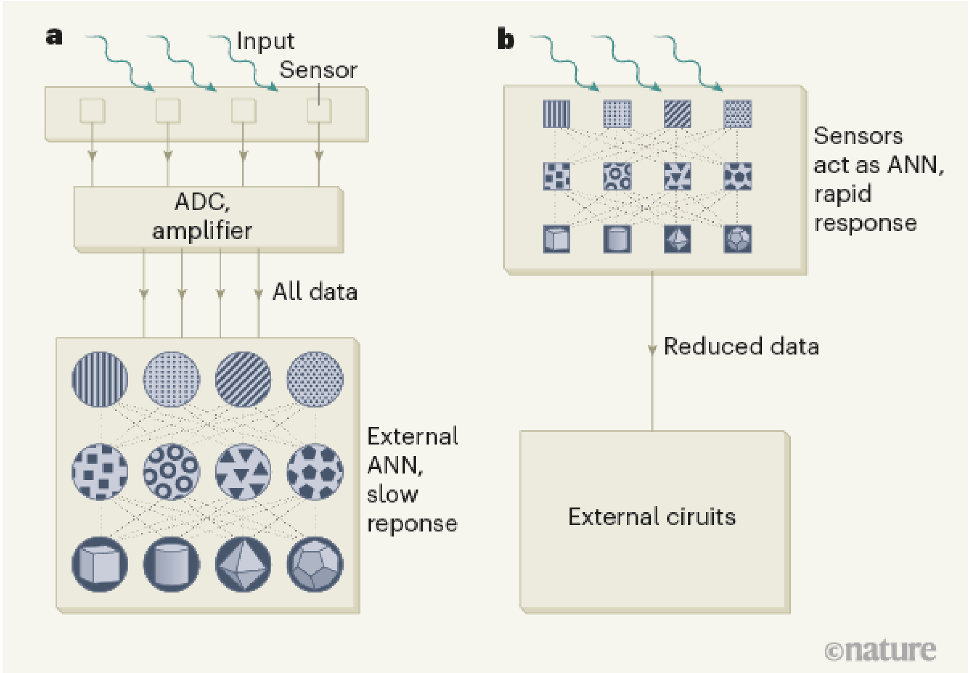
- Physical neural networks: Artificial neurons, artificial synapses



van de Burgt, et al. *Nat. Mater.* **2017**, *16*, 414.

Reducing Data Transfer to Improve Vision Sensor Response Time



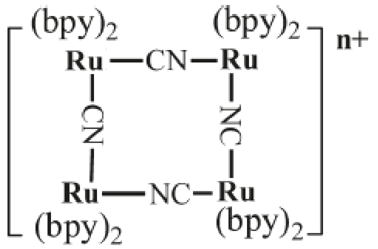
Nature **2020**, *579*, 32.

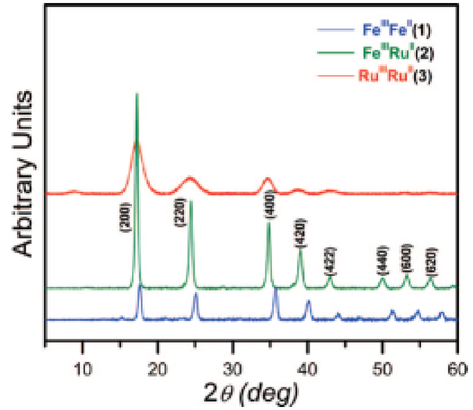
Mennel et al., *Nature* **2020**, *579*, 62.

Ruthenium Prussian Blue Analogue (RuPBA)

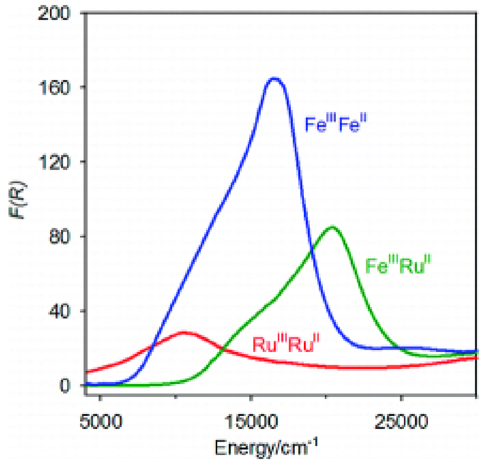
- Ruthenium Prussian blue analogue (RuPBA) has the highest measured DC conductivity and lowest IVCT energy of the PBA family.

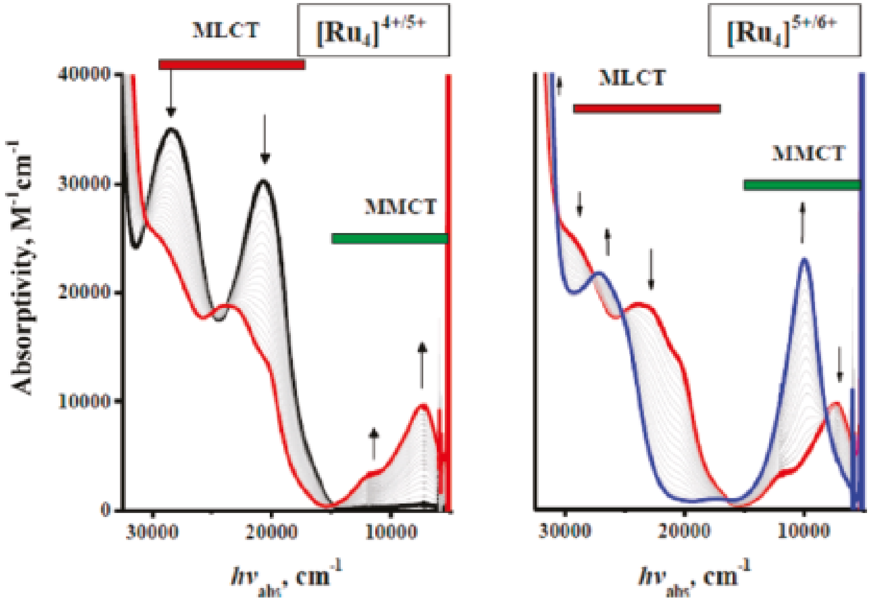
Molecular analogue of RuPBA





Intervalence charge transfer (IVCT)





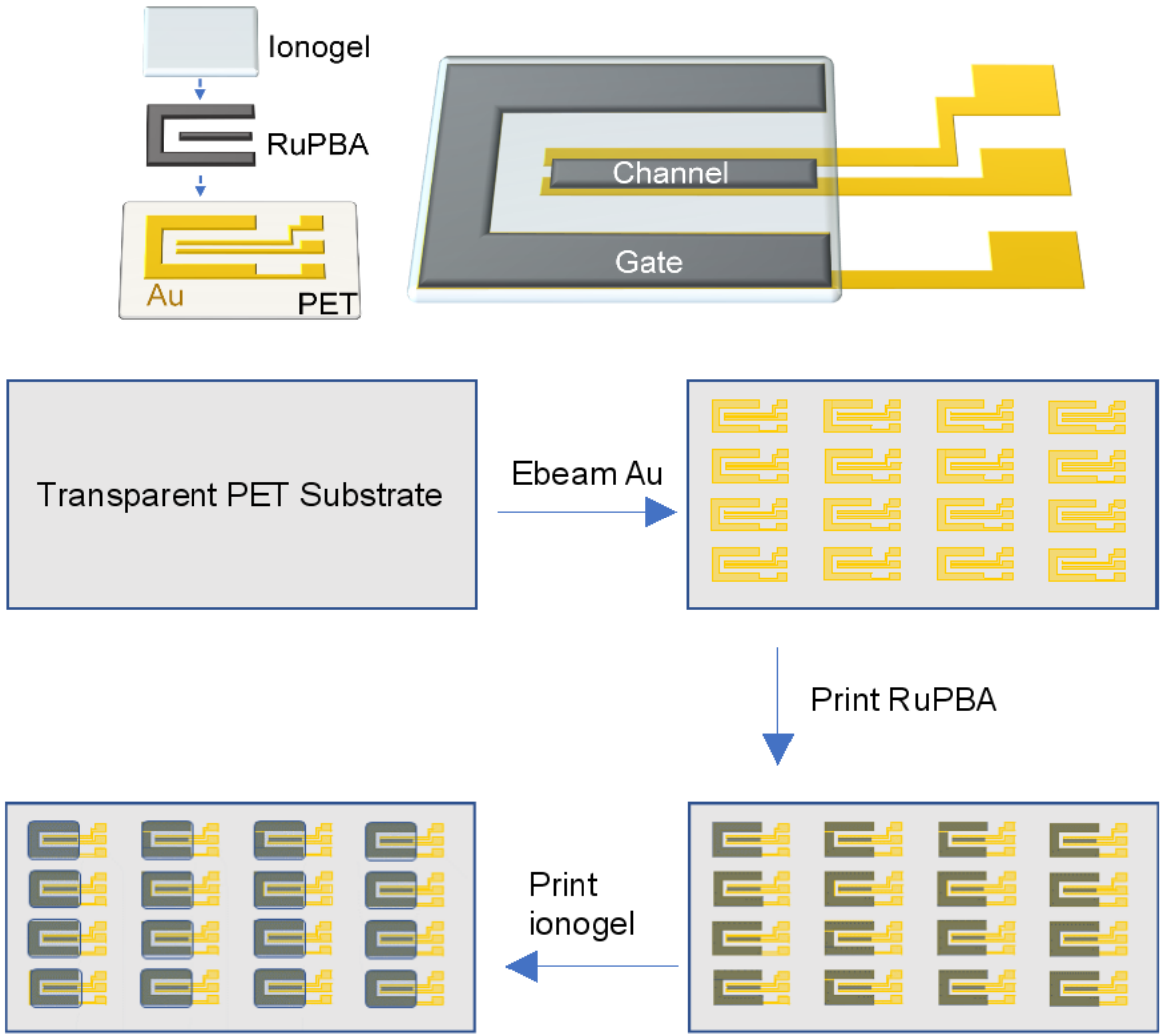
Lin et al., *Inorg. Chem.* **2011**, *50*, 8274.

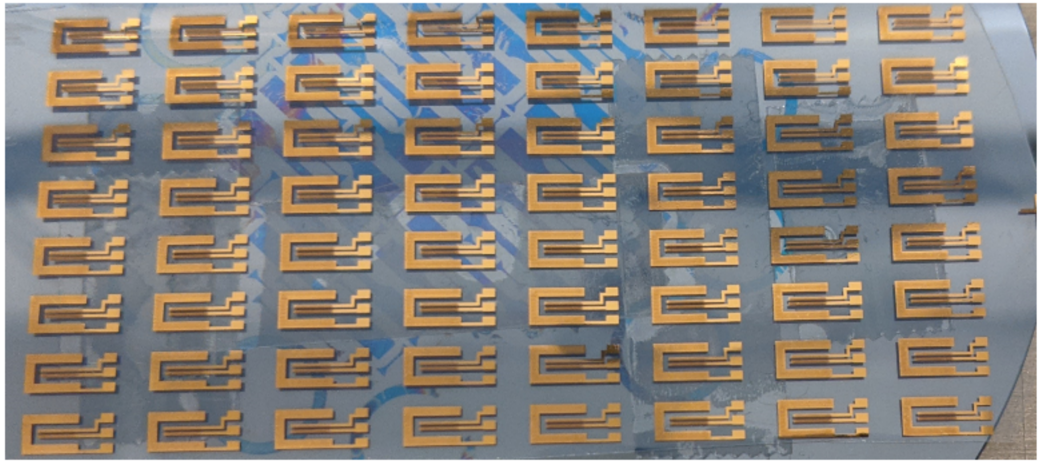
compound	lattice constant (Å)	band manifold (cm^{-1})	electrical conductivity[d] (S/cm)
$Fe_4[Fe(CN)_6]_3 \cdot 14H_2O$ (**1**)	10.16	16 210	5.57×10^{-5}
$Fe_4[Ru(CN)_6]_3 \cdot 18H_2O$ (**2**)	10.42	20 180	5.05×10^{-6}
$K_{1.2}Ru_{3.6}[Ru(CN)_6]_3 \cdot 16H_2O$ (**3**)	~10.6[e]	9980	5.69×10^{-3}

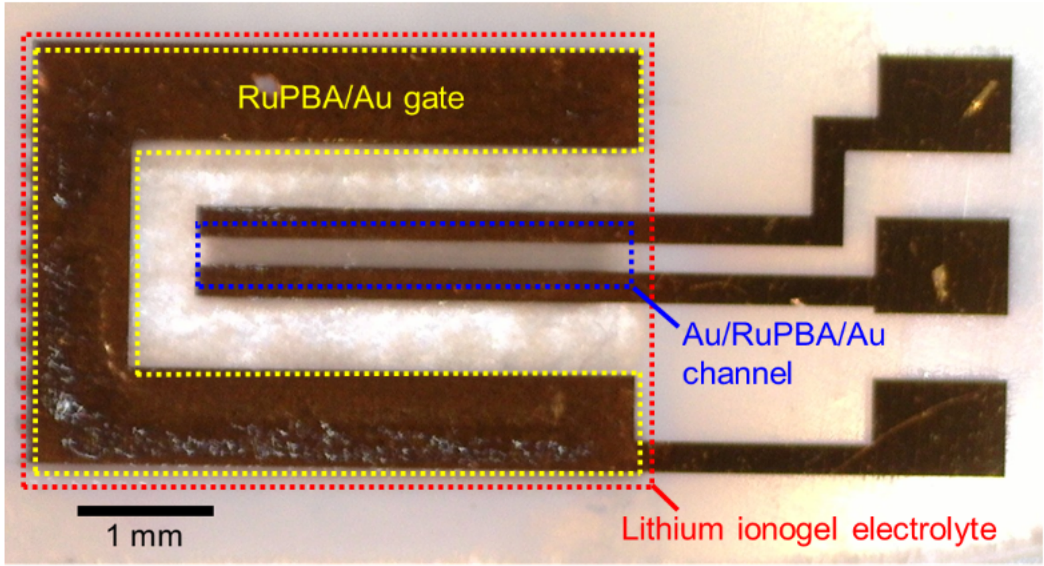
- Molecular analogues exhibit Class II/III properties (localized-delocalized transition).

Behera et al., *Chem. Mater.* **2009**, *21*, 1922.

RuPBA ECRAM Device Fab/Architecture

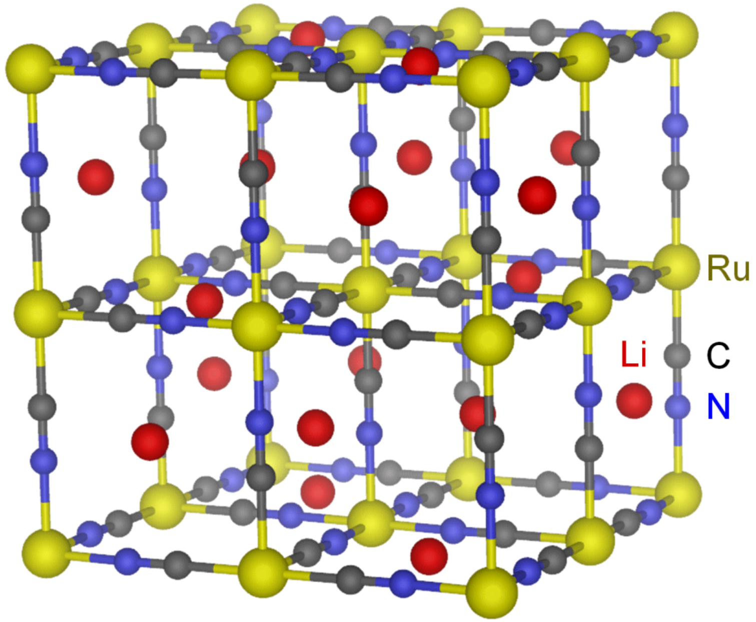


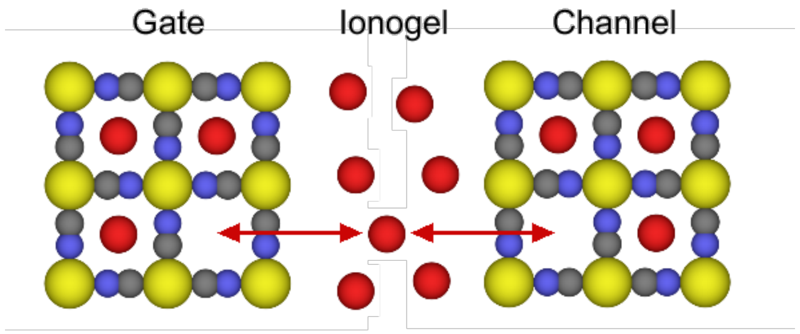




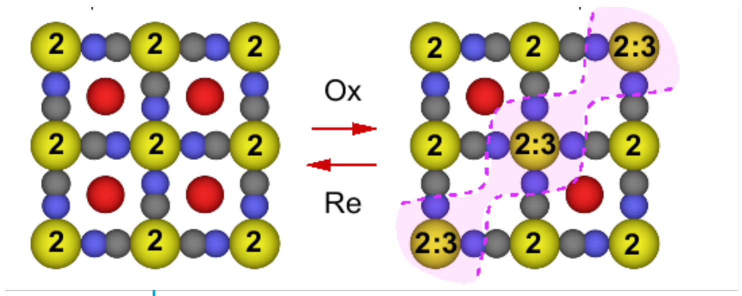
Robinson, et al. *arXiv preprint* **2022**, [DOI: 10.48550/arXiv.2207.07756]

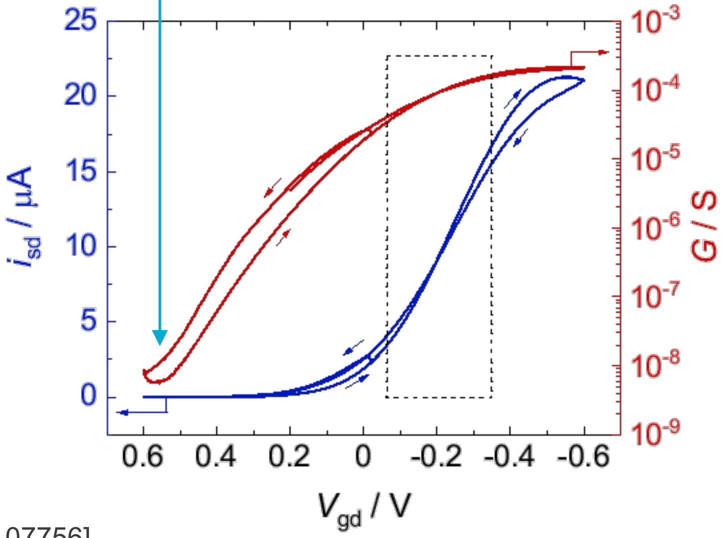
Steady State Transfer Characteristics



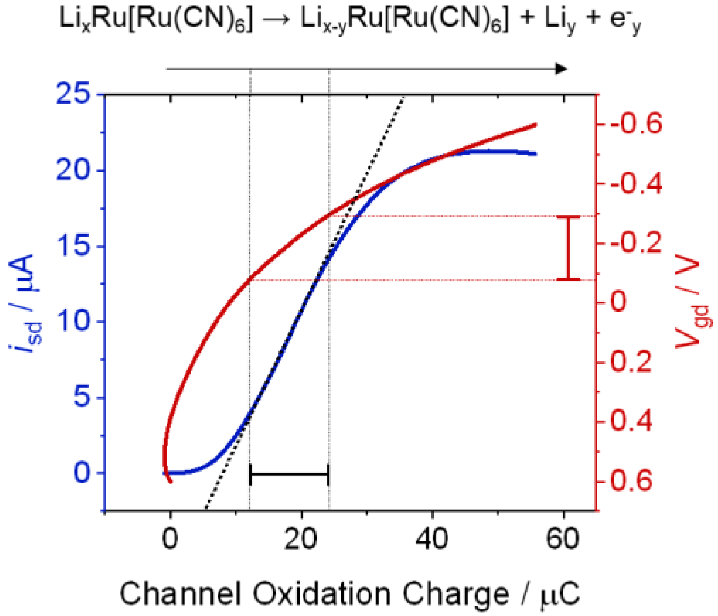


ECRAM Device Channel



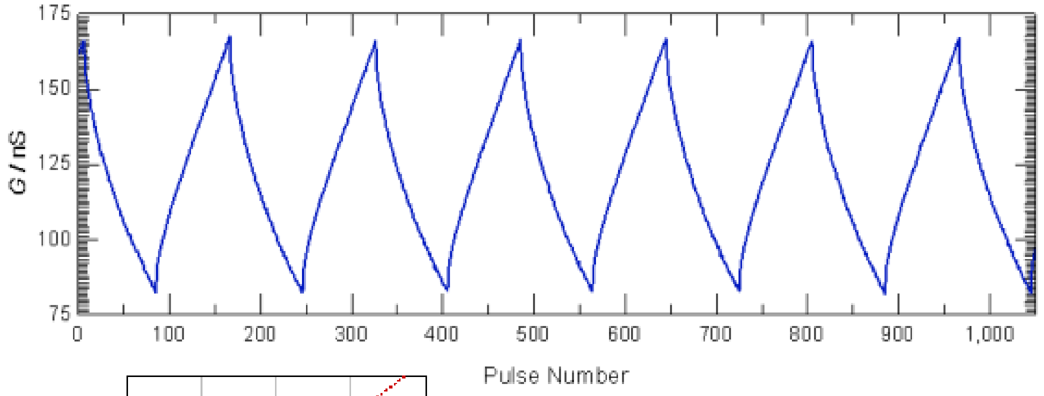


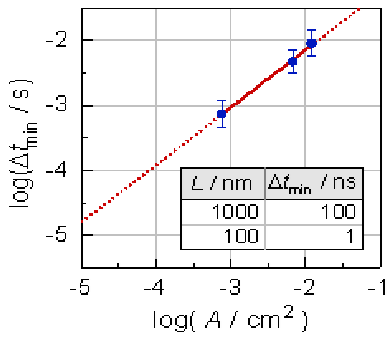
- P-type, holes as principle carriers
- 4 orders of magnitude tunability in conductance
- Linear relationship with faradaic charge
  - Stored charge → stored conductance
  - Ideal for programming synapses

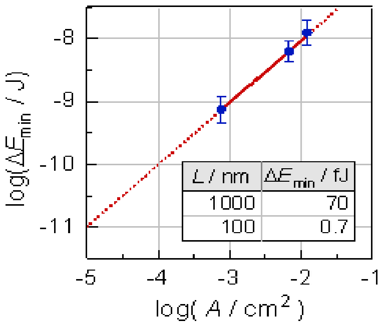


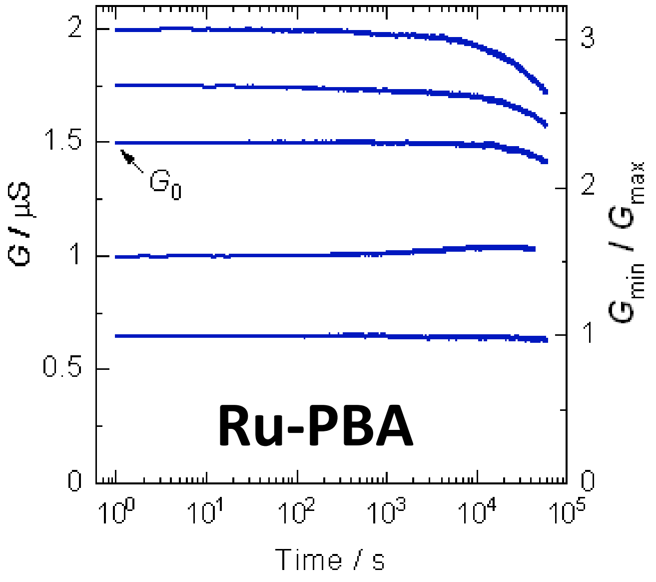
Robinson, et al. *arXiv preprint* **2022**, [DOI: 10.48550/arXiv.2207.07756]

ECRAM Device Performance

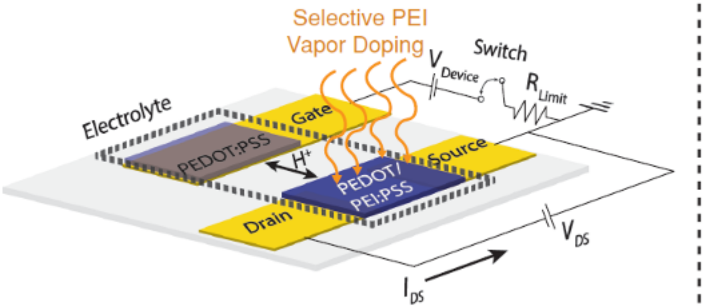


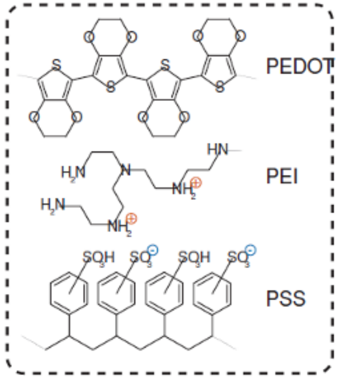


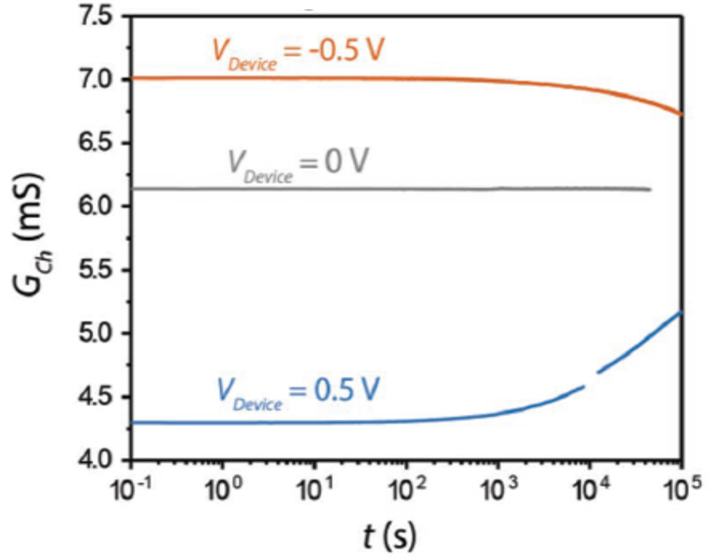




Robinson, et al. *arXiv preprint* **2022**, [DOI: 10.48550/arXiv.2207.07756]



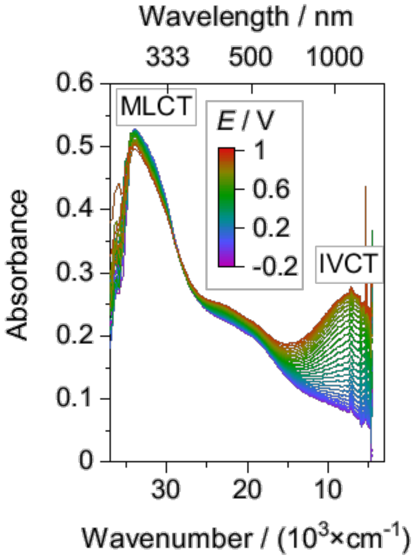


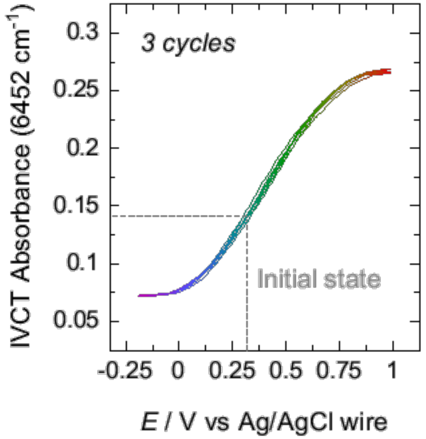


van de Burgt, et al. *Nat. Mater.* **2017**, *16*, 414.
S. T. Keene, et al. *Adv. Electron. Mater.* **2019**, *5*, 1800686.
Fuller, et al. *Science* **2019**, *364*, 570.

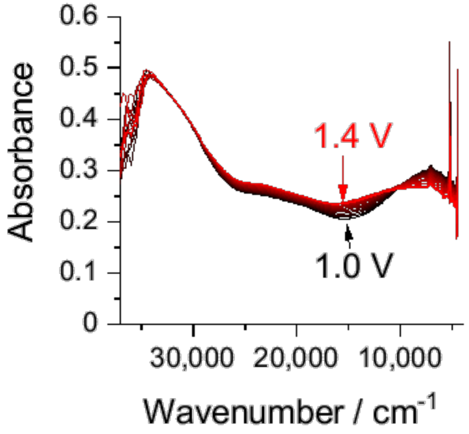
UV/Vis/NIR Spectroscopy

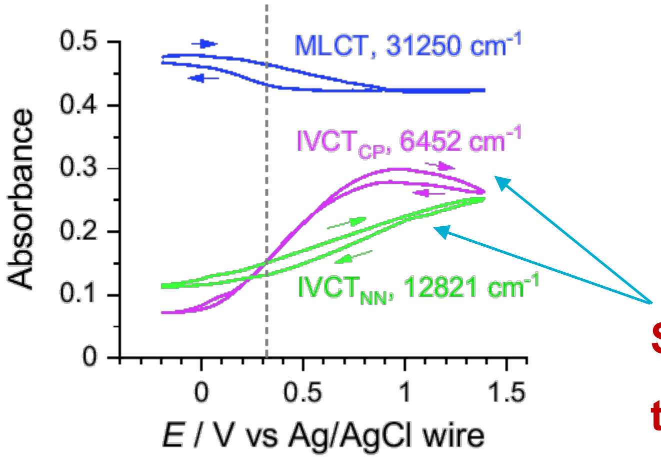
Reversible Range

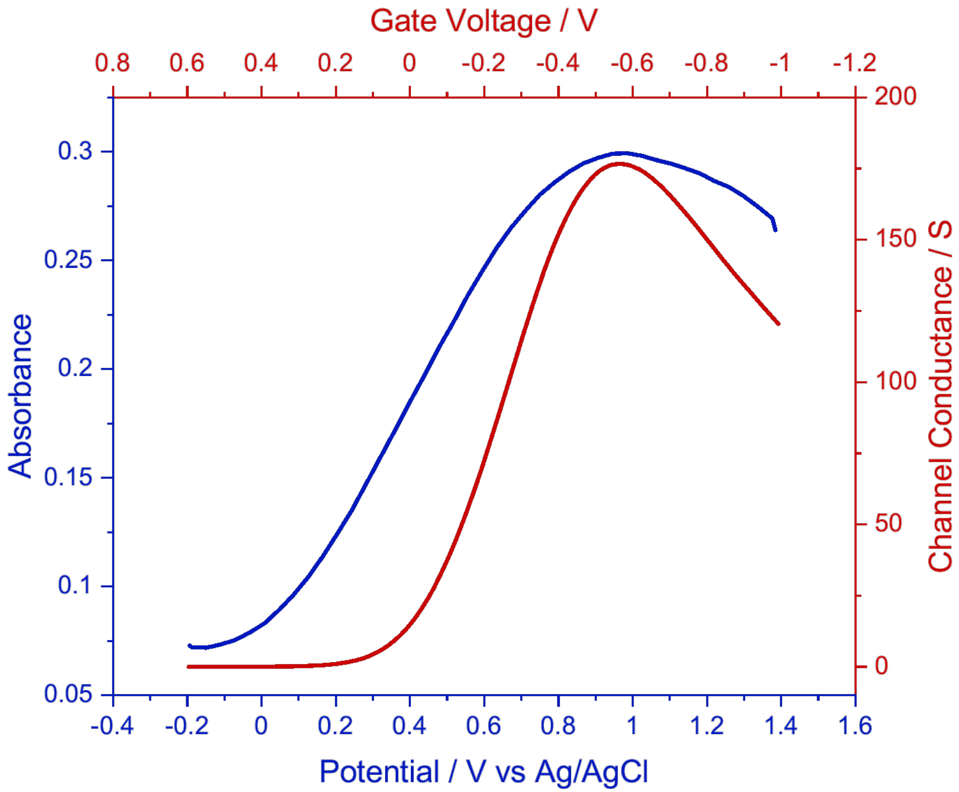




Higher RuPBA Oxidation States



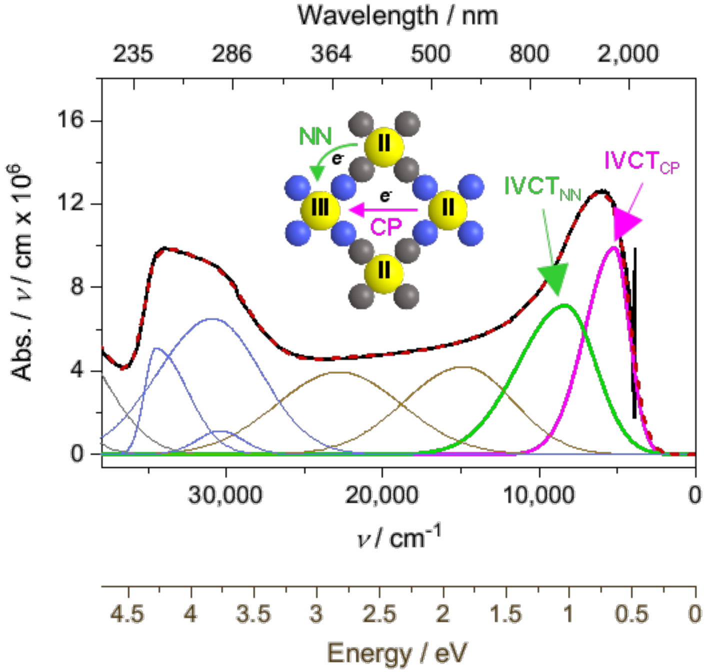


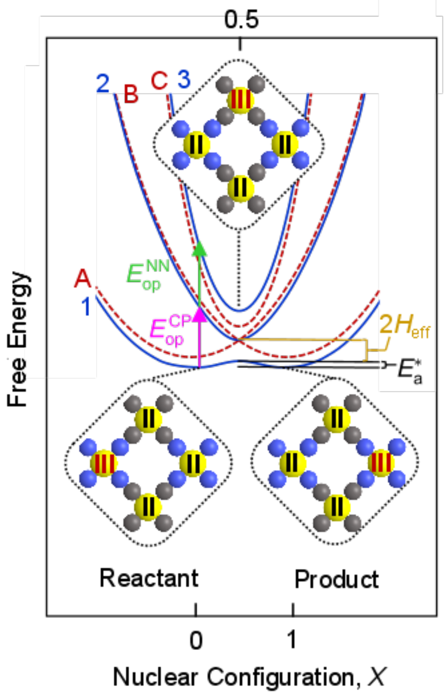


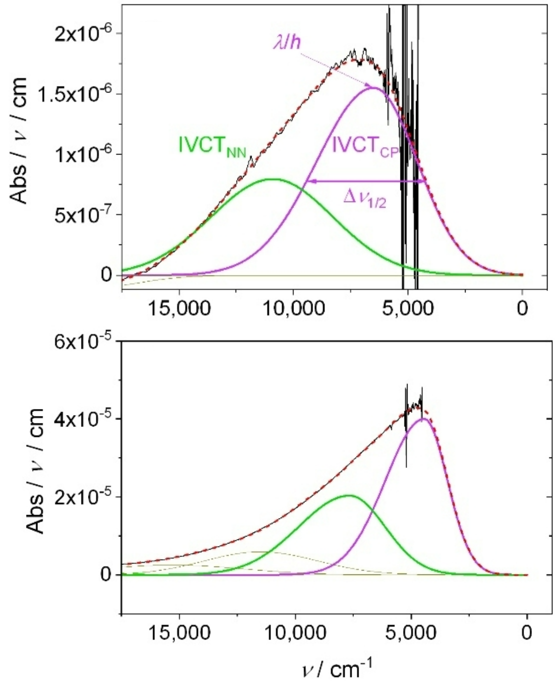
Spectroelectrochemical trends indicate more than one IVCT pathway.

Robinson, et al. *arXiv preprint* **2022**, [DOI: 10.48550/arXiv.2207.07756]

Spectroscopic Insight into Conduction Mechanism







E = 0 V

E = 1 V

$$\Delta\nu_{1/2} = [4\ln(2)\lambda k_B T]^{1/2} + \lambda - 2H_{eff}$$

$$E_a^* = \frac{(\lambda - 2H_{eff})^2}{4\lambda}$$

$$k_{ct} = \kappa\nu_n \exp(-E_a^*/k_B T)$$

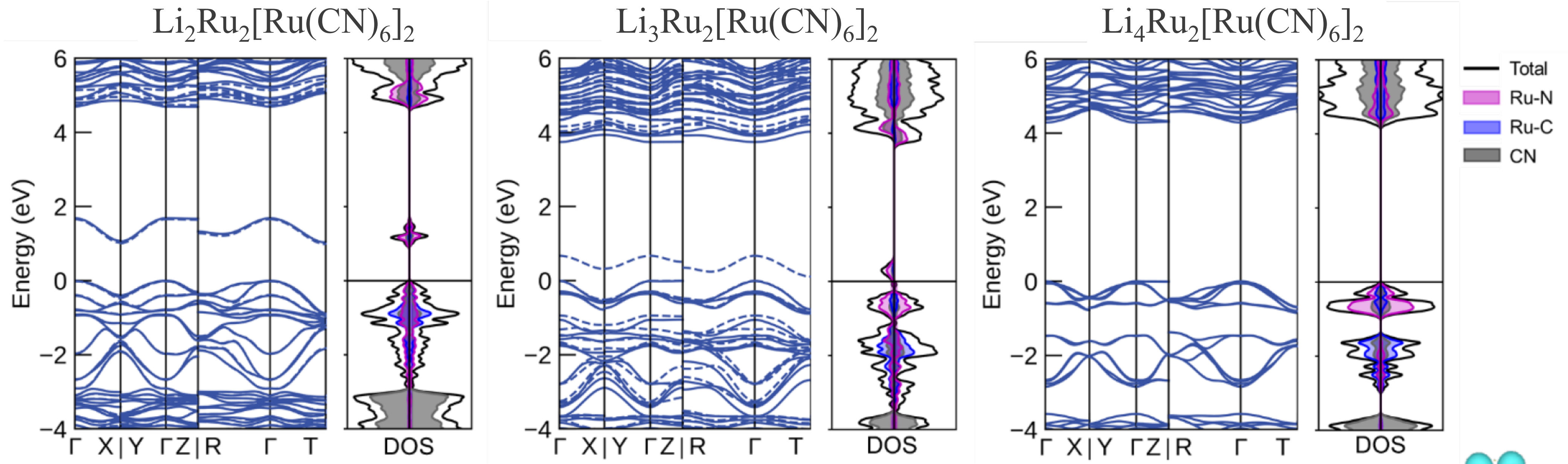
$$\mu_h = ed^2 k_{ct}/2k_B T$$

Approximated Parameters Derived from Crosspore IVCT Analysis

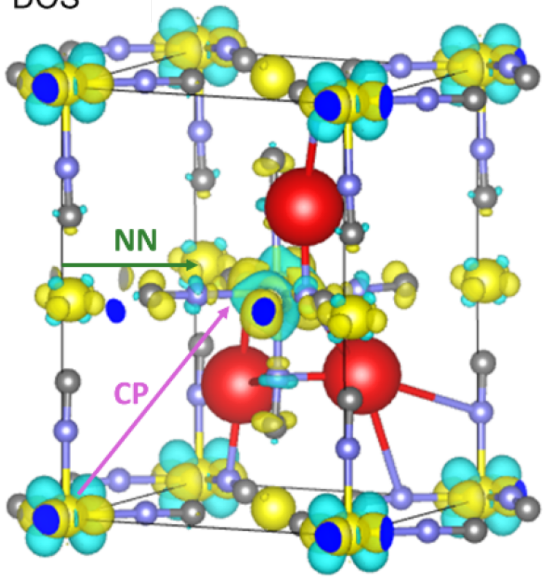
E / V	λ / eV	$h\Delta\nu_{1/2}$ /eV	H_{eff} / eV	E_a^* / meV	ν_{el} / 10^{14}s^{-1}	k_{ct} / 10^{12}s^{-1}	μ_h / cm^{2}V^{-1}s^{-1}
0.00	0.81	0.64	0.20	50	7.6	8.9	0.95
0.05	0.76	0.50	0.25	24	12	25	2.7
0.10	0.74	0.45	0.26	16	13	34	3.7
0.15	0.66	0.39	0.24	11	12	41	4.3
0.30	0.59	0.36	0.22	11	10	42	4.5
0.60	0.51	0.34	0.18	11	7.5	41	4.3
1.00	0.55	0.39	0.18	17	7.3	33	3.5

B. S. Brunschwig, C. Creutz, N. Sutin, *Chem. Soc. Rev.* **2002**, *31*, 168.
M. B. Robin, P. Day, in *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 10 (Eds: H. J. Emeléus, A. G. Sharpe), Academic Press, 1968.
Robinson, et al. *arXiv preprint* **2022**, [DOI: 10.48550/arXiv.2207.07756]

Mechanism: DFT Computation



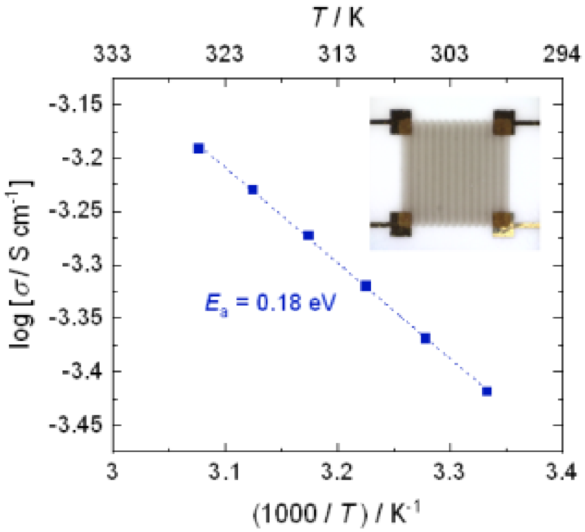
Ru Formal Oxidation State	Lattice Constants (Å)			Band Gap (eV)		Effective Mass
	a	b	c	direct	indirect	
2.5	7.269	7.293	10.334	1.26	0.98	0.70
2.25	7.415	7.217	10.295	0.50	0.10	0.41
2	7.543	7.038	10.180	4.29	4.29	0.52

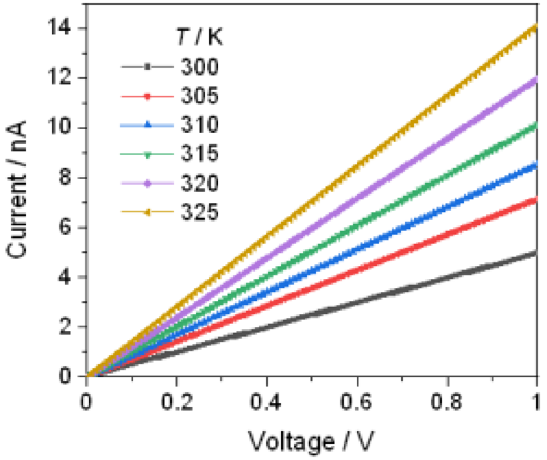


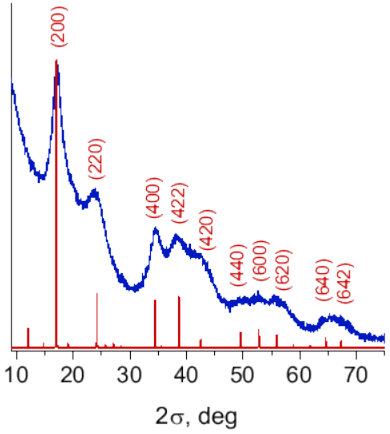
- **$Li_3Ru_2[Ru(CN)_6]_2$ predicted to have a hole mobility of 5 cm V^{-1} s^{-1}, compared to 4 cm V^{-1} s^{-1} determined spectroscopically.**

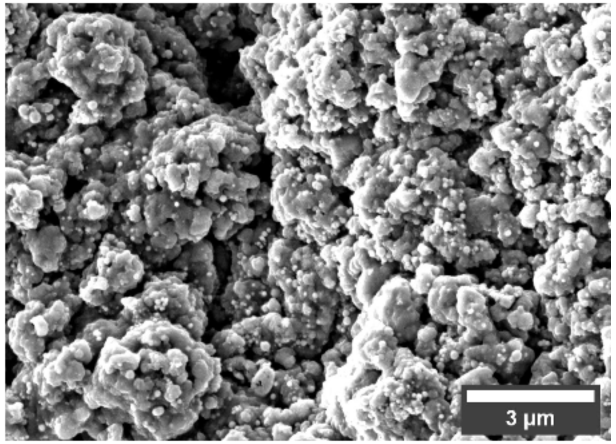
Robinson, et al. *arXiv preprint* **2022**, [DOI: 10.48550/arXiv.2207.07756]

Challenges Going Forward









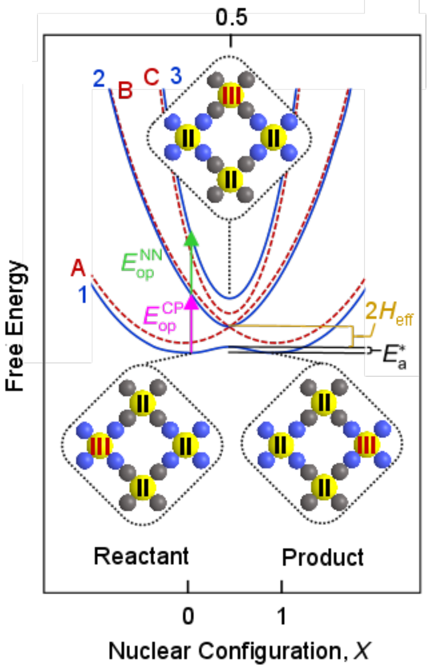
- Activation energy is relatively low for a PBA, but ~10x higher than predicted.
- Charge transfer at grain boundaries likely requires larger activation energy than in bulk.

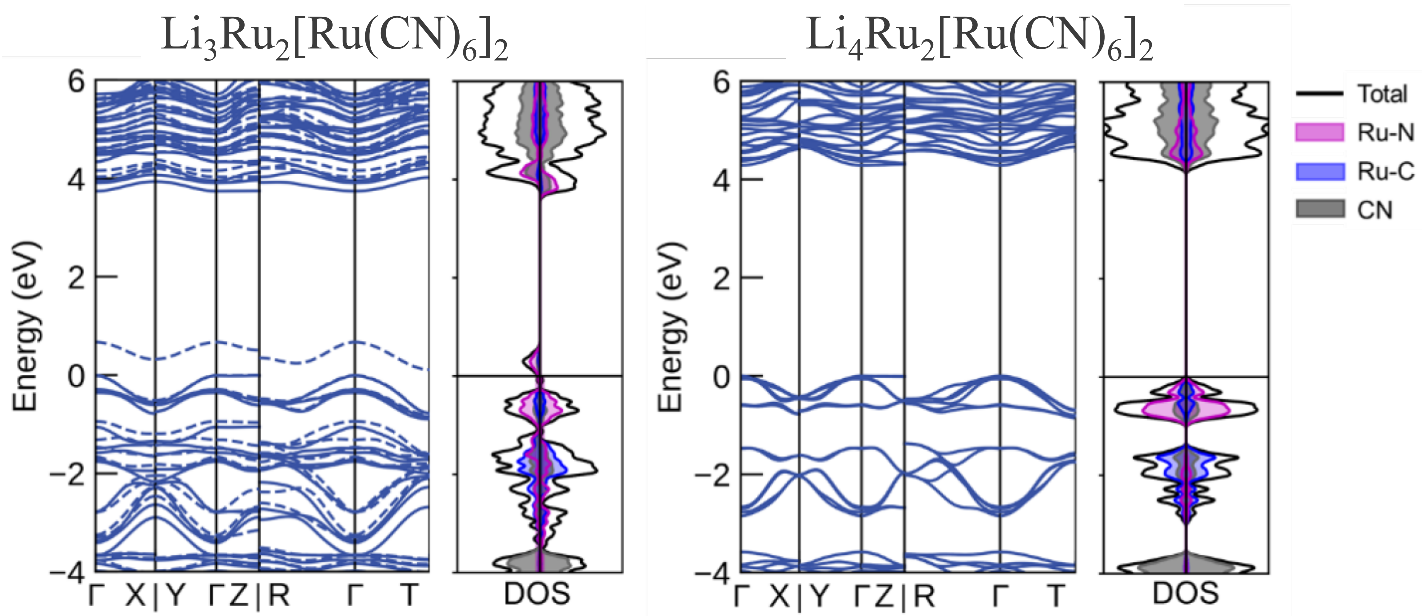
Robinson, et al. *arXiv preprint* **2022**, [DOI: 10.48550/arXiv.2207.07756]

Conclusion

- New potential application for extended coordination compounds such as PBAs in neuromorphic computing via ECRAM.

- Working hypothesis for nearest-neighbor and cross-pore IVCT pathways involved in electron hole concentration and mobility, supported by DFT and electron transfer theory.





Robinson, et al. *arXiv preprint* **2022**, [DOI: 10.48550/arXiv.2207.07756]

Acknowledgements

Funding

- Sandia National Laboratories Directed Research and Development Program

Coworkers

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, A. Alec Talin

Helpful discussions

- Jeffrey R. Long, UC Berkeley
- Deanna D'Alessandro, University of Sydney

Thank you!