Molecular Quantum-dot Cellular Automata

Craig S. Lent
University of Notre Dame

ND Collaborators:

Greg Snider (EE)
Alex Kandel (Chem)
Ken Henderson (Chem)
Thomas Fehlner (Chem)
Yuhui Lu (EE & Chem)
Erik Blair (EE)
Alexei Orlov (EE)
Mike Niemier (CS)

International Collaborators:

Claude Lapinte (Chem, Univ. of Rennes, France)
Ismo Hänninen (Computer Science, Univ. of Tampere, Finland)
Konrad Walus, (EE, Univ. of British Columbia, Canada)

Supported by National Science Foundation

Outline of presentation

- Quantum-dot Cellular Automata
  - Motivation
  - Basic operations
  - Realizations
- Clocked molecular QCA
  - Theory
  - Measurement
- Synthesis of candidate molecules

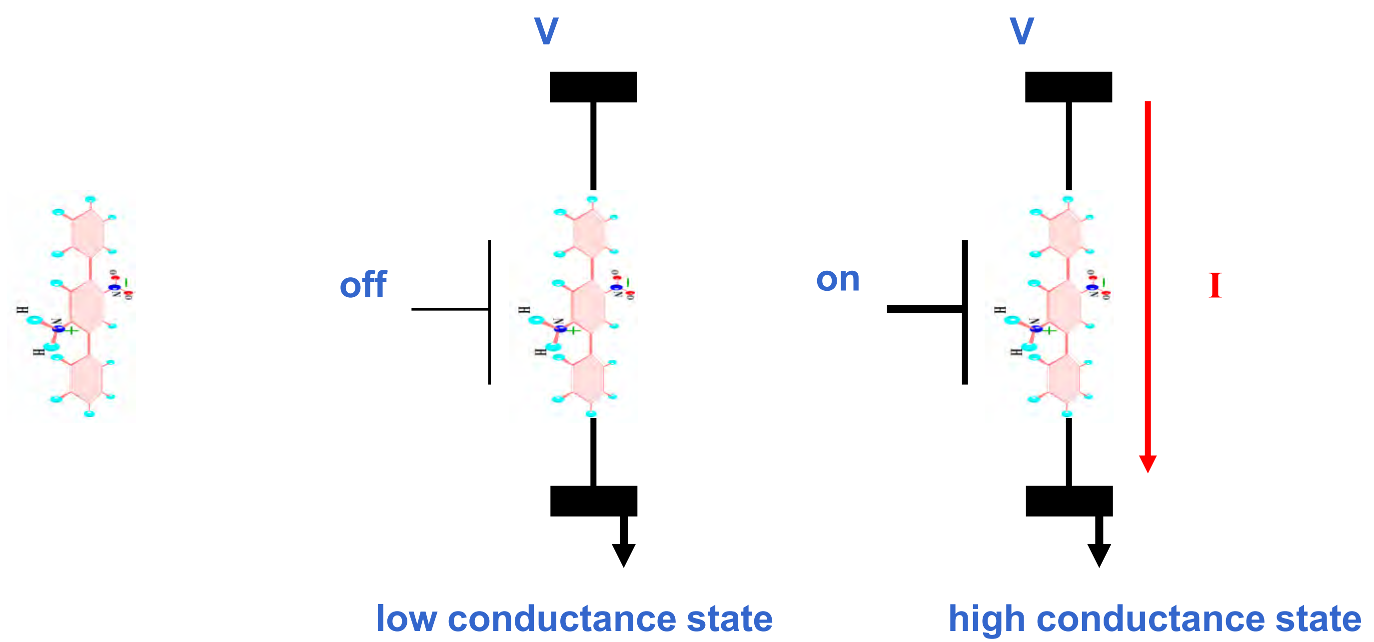
Requirements for integrated molecular devices

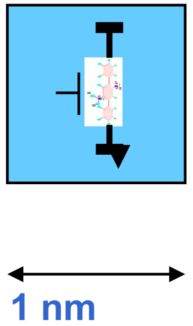
- Ultra-low power dissipation
- Nano-integration: connect many devices together
- Power gain: must restore signal levels stage-to-stage
- Robustness: overcome variations and defects

Power dissipation

Power dissipation is the main limiter.

Dream molecular transistors



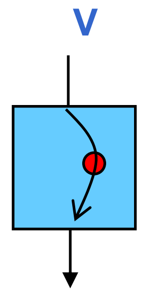


f_{max}=1 THz

Molecular densities: 1nm x 1nm → $10^{14}/cm^2$

Transistors at molecular densities

Suppose in each clock cycle a *single* electron moves from power supply (1V) to ground.



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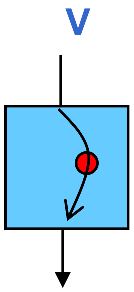
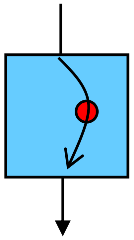


Power dissipation (Watts/cm^2)

Frequency (Hz)	10^{14} devices/cm^2	10^{13} devices/cm^2	10^{12} devices/cm^2	10^{11} devices/cm^2
10^{12}	16,000,000	1,600,000	160,000	16,000
10^{11}	1,600,000	160,000	16,000	1,600
10^{10}	160,000	16,000	1,600	160
10^{9}	16,000	1600	160	16
10^{8}	1600	160	16	1.6
10^{7}	160	16	1.6	0.16
10^{6}	16	1.6	0.16	0.016

ITRS roadmap:
7nm gate length, 10^9 logic transistors/cm^2 @ 3×10^{10} Hz for 2016

Transistors at molecular densities



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10^{10}	160,000	16,000	1,600	160
10^{9}	16,000	1600	160	16
10^{8}	1600	160	16	1.6
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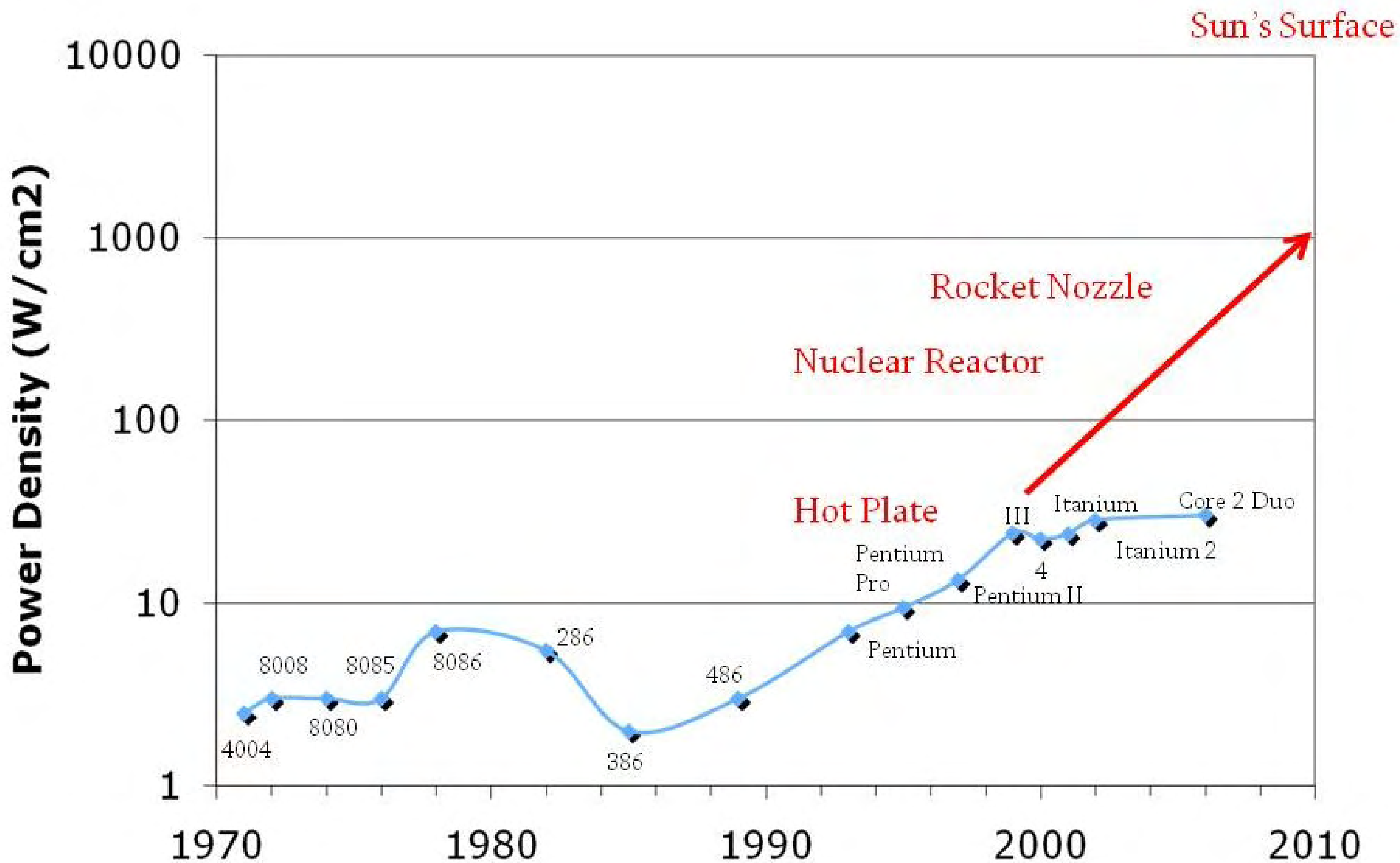
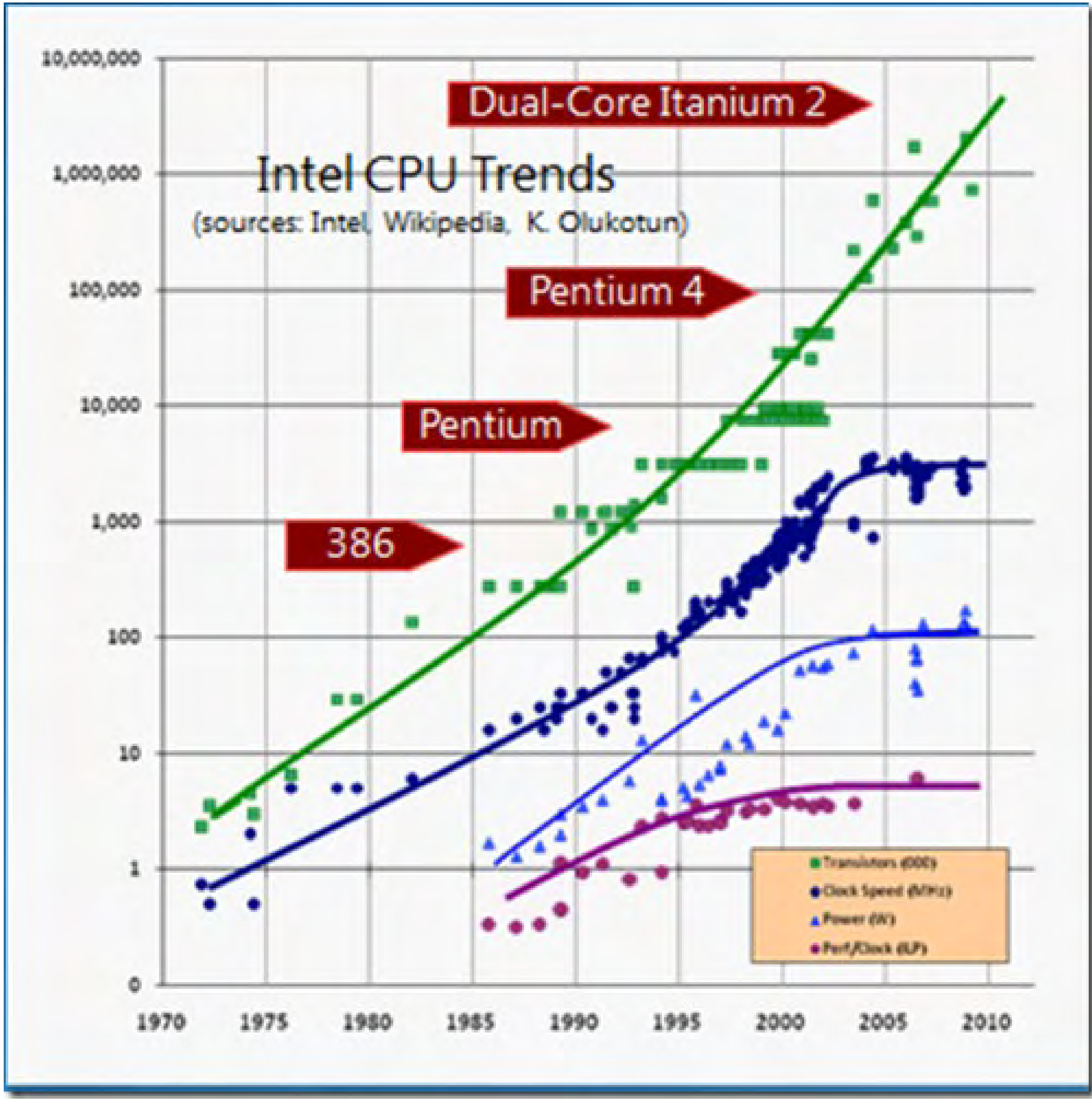
ITRS roadmap:
7nm gate length, 10^9 logic transistors/cm^2 @ 3×10^{10} Hz for 2016

Power Density



(Robin Joyce)

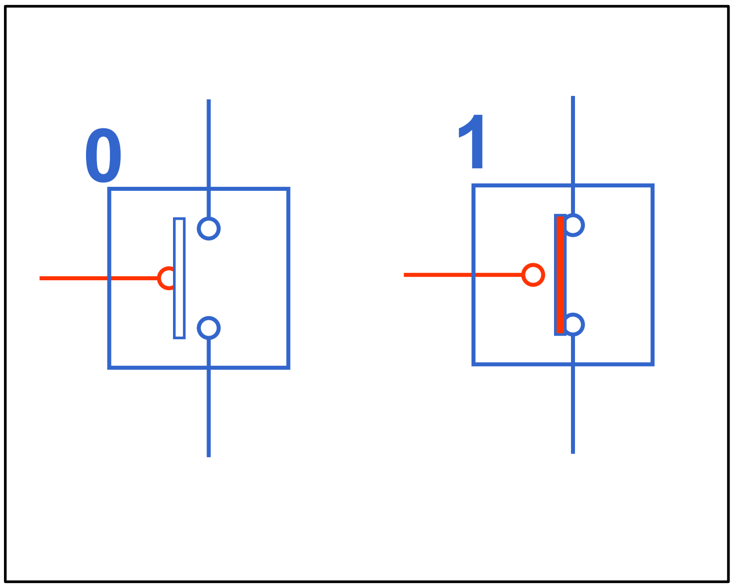
Trends



Heat limits clock speed

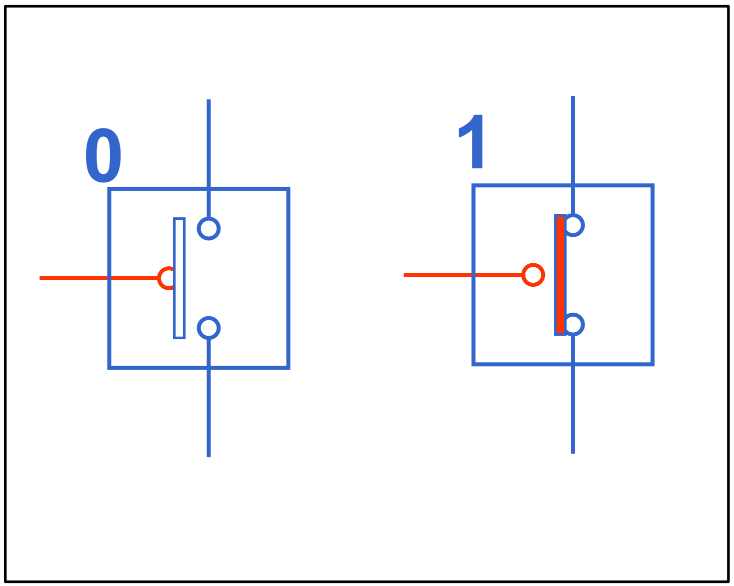
Solution: Change the way information is represented

Current switch

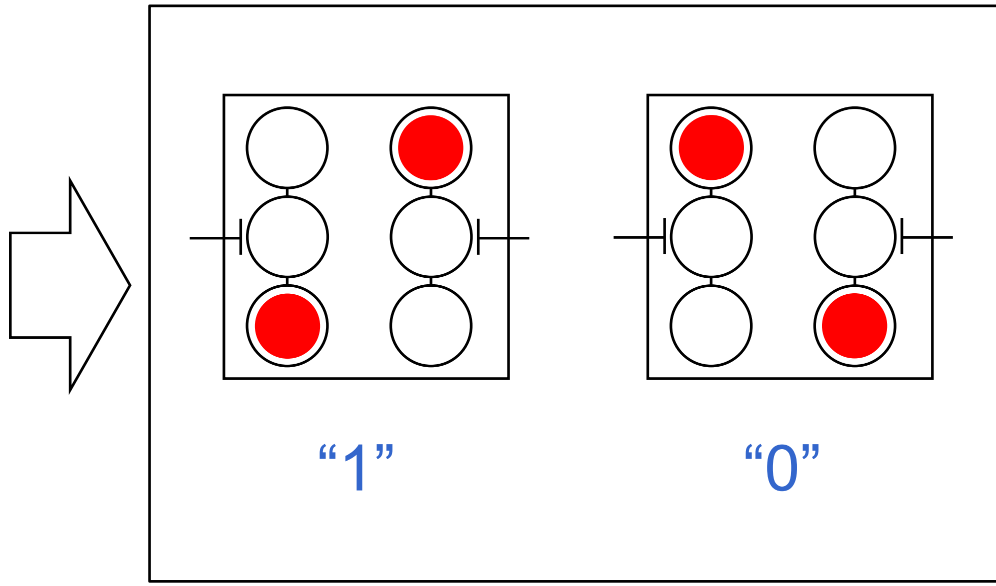


Solution: Change the way information is represented

Current switch

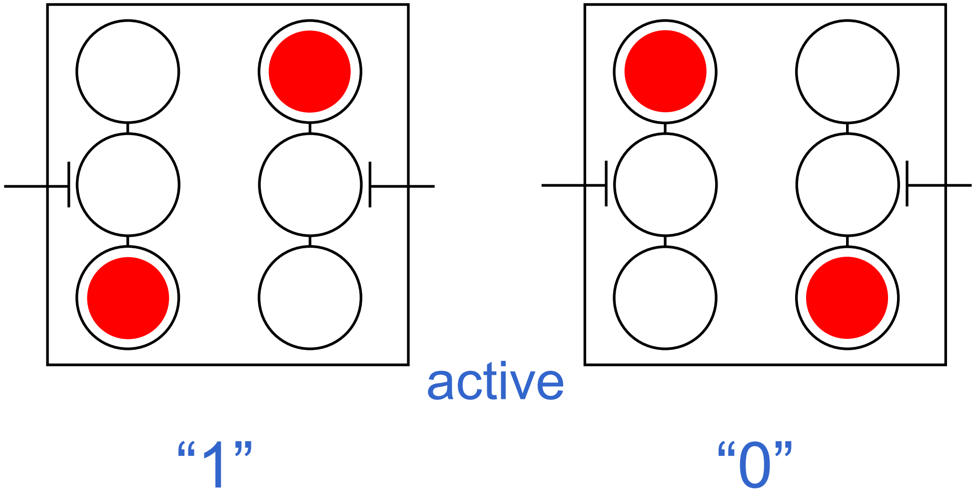


Charge configuration



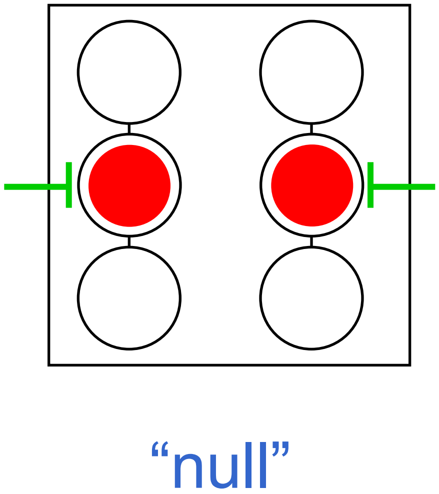
Quantum-dot cellular automata

Represent binary information by charge configuration of cell.



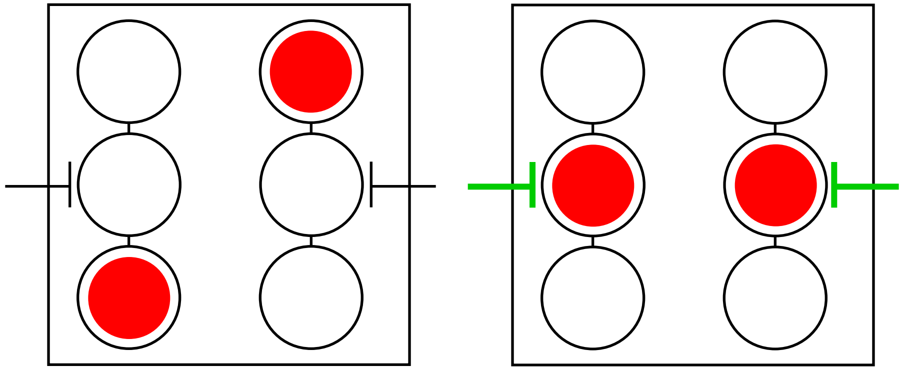
QCA cell

- Dots localize charge
- Two mobile charges
- Tunneling between dots
- Clock signal varies relative energies of “active” and “null” dots



Quantum-dot cellular automata

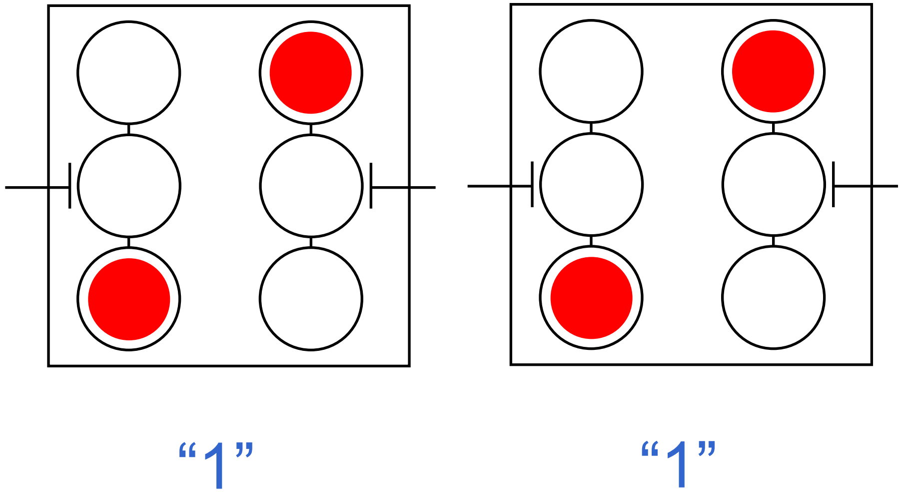
Neighboring cells tend to align in the same state.



“1” “null”

Quantum-dot cellular automata

Neighboring cells tend to align in the same state.



Quantum-dot cellular automata

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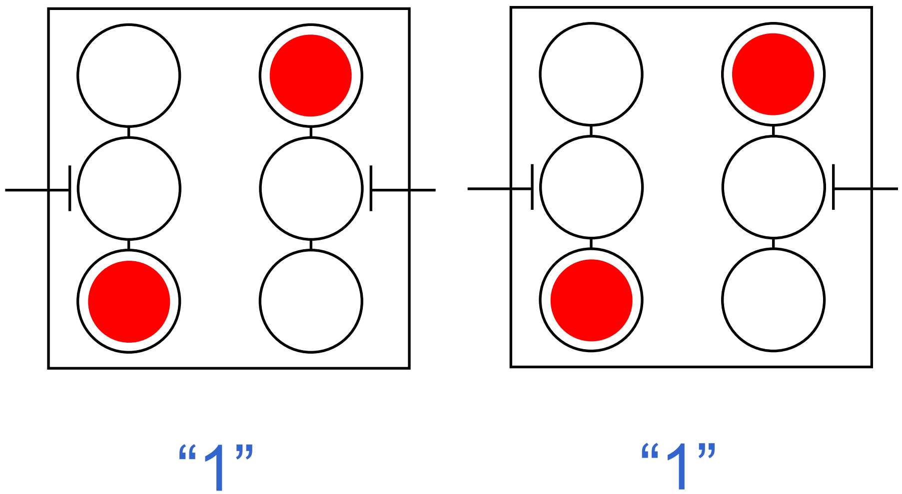
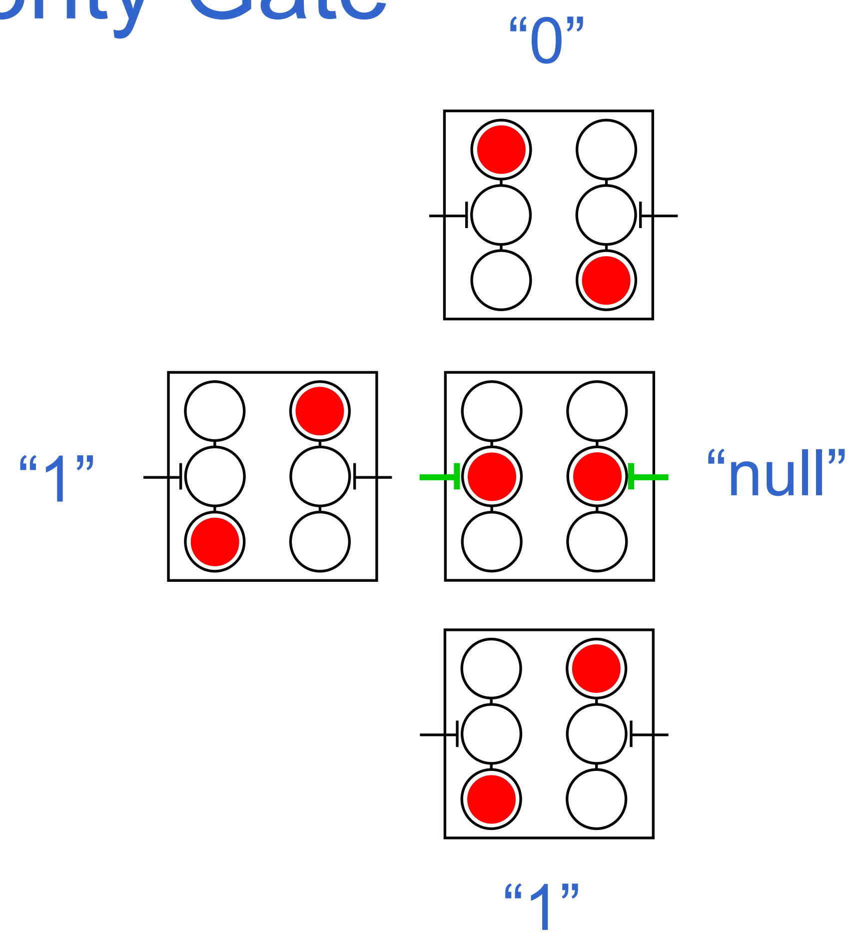
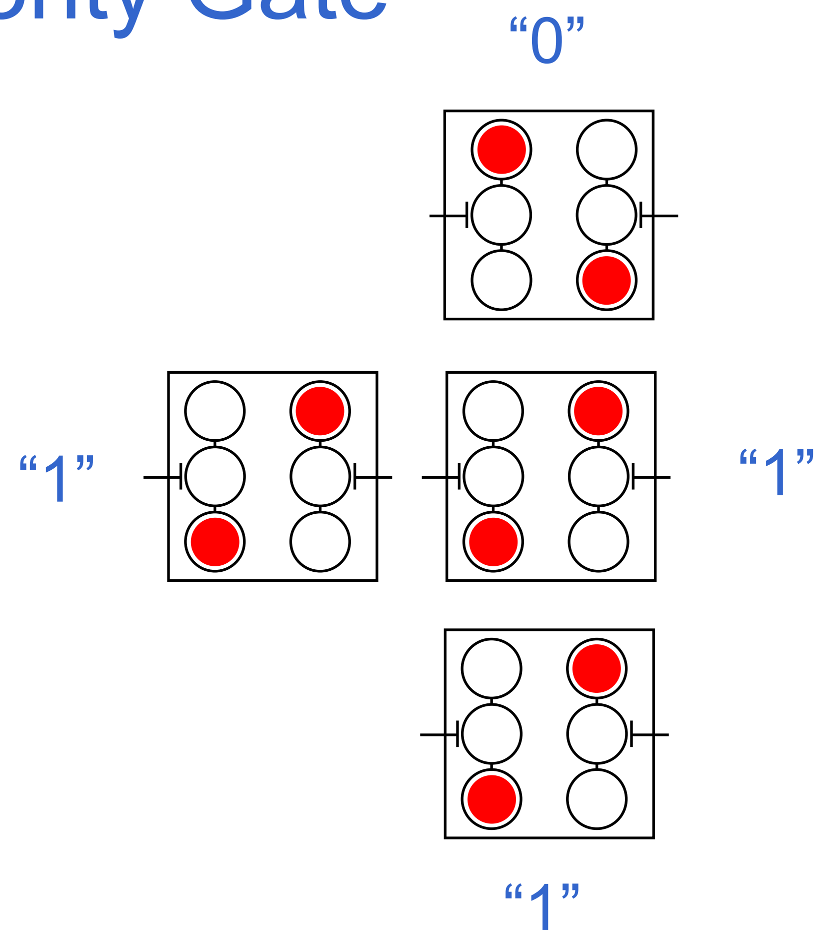


This is the COPY operation.

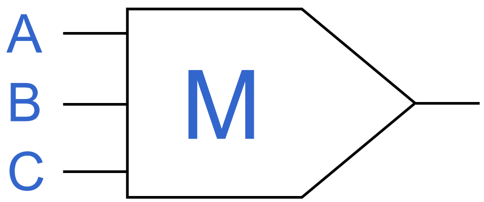
Majority Gate



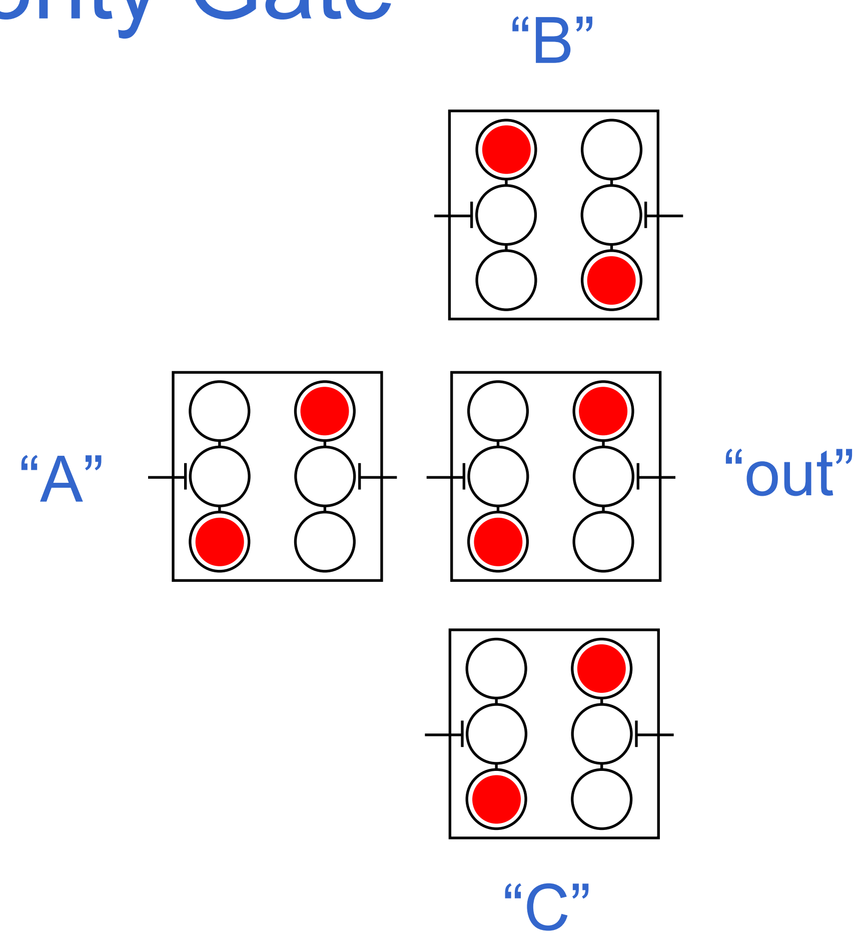
Majority Gate



Majority Gate

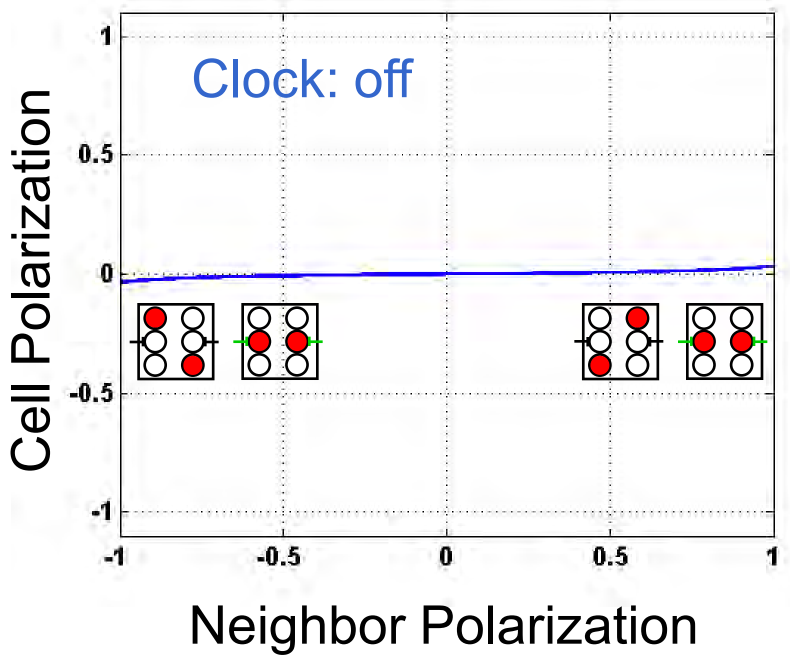


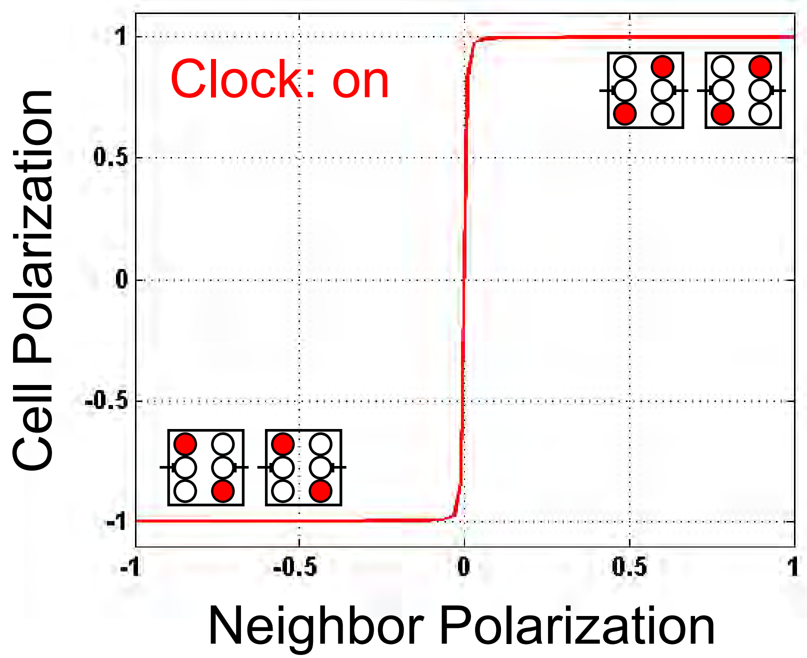
	A	B	C	Output
AND gate	0	0	0	0
	0	0	1	0
	0	1	1	1
	0	1	0	0
OR gate	1	1	0	1
	1	1	1	1
	1	0	1	1
	1	0	0	0



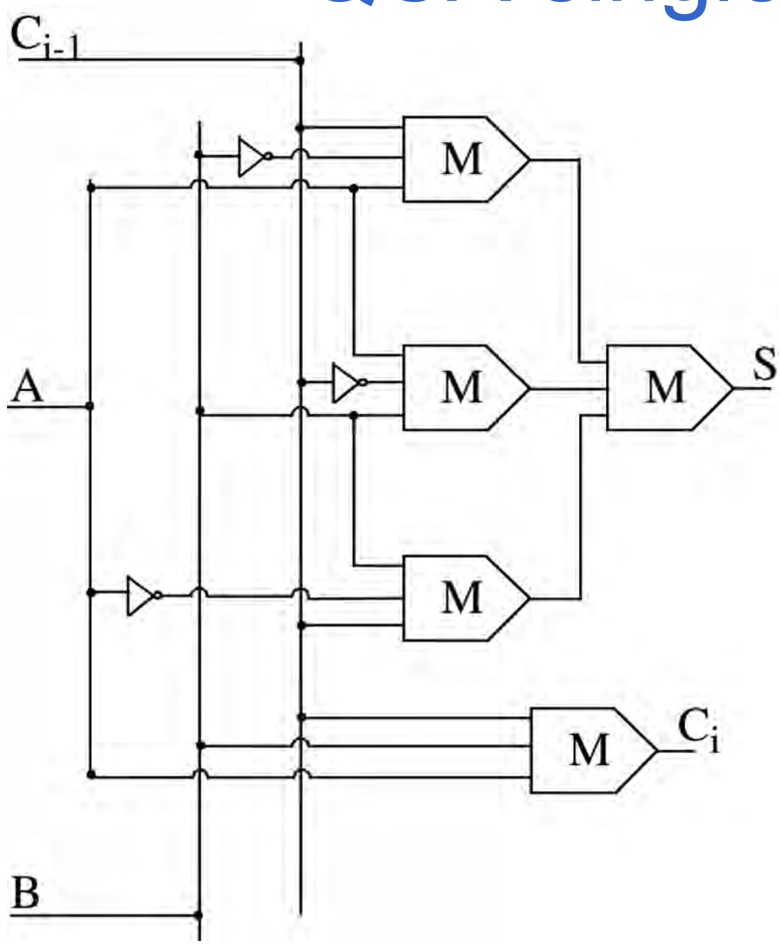
Three input majority gate can function as programmable 2-input AND/OR gate.

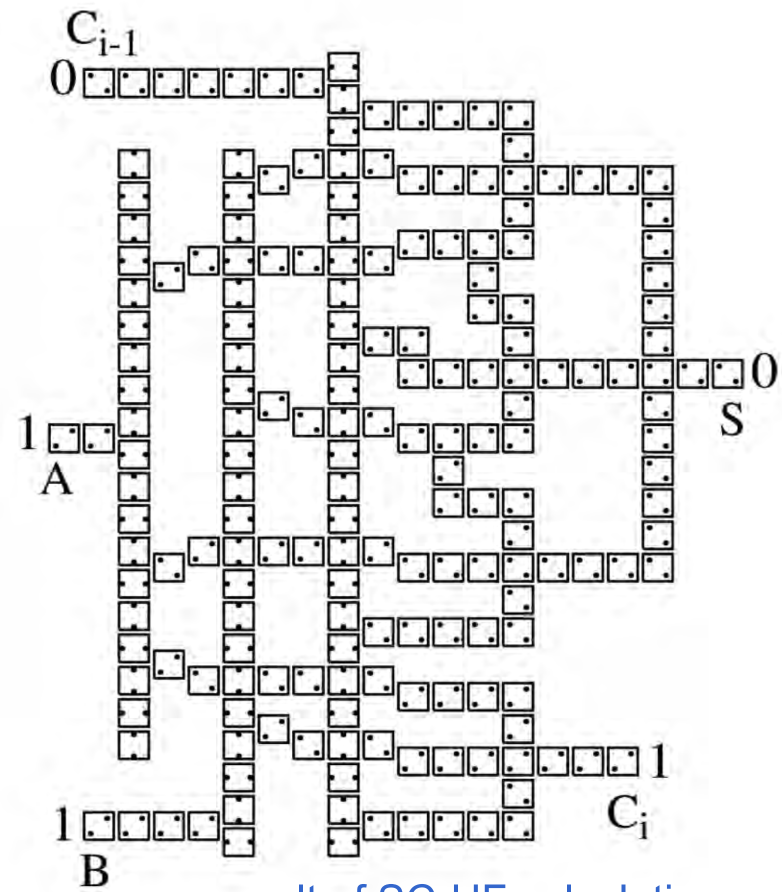
QCA cell-cell response function





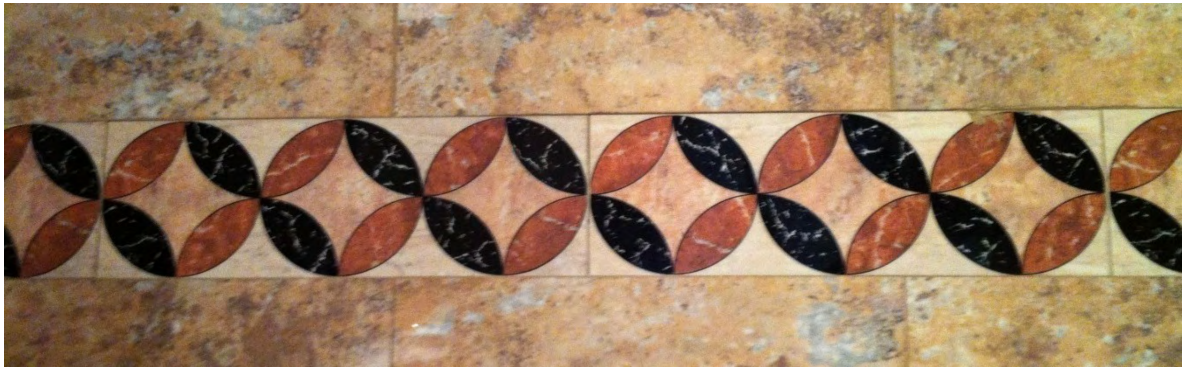
QCA single-bit full adder

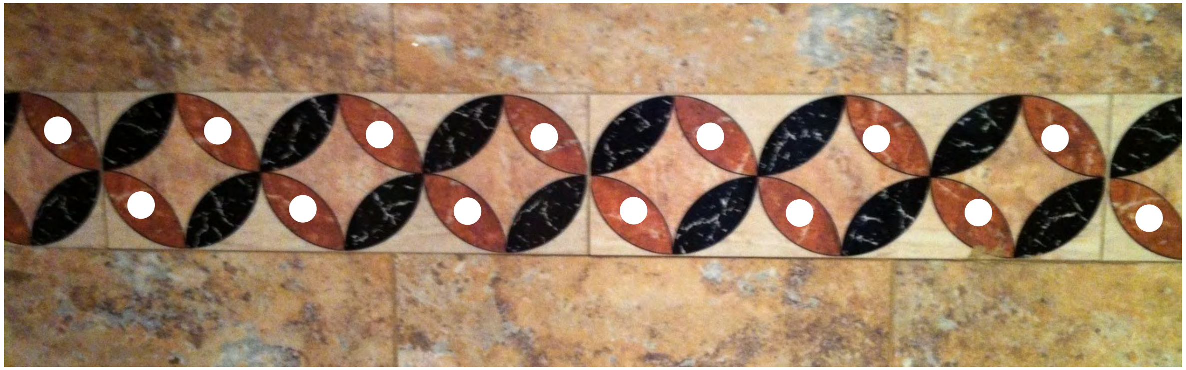




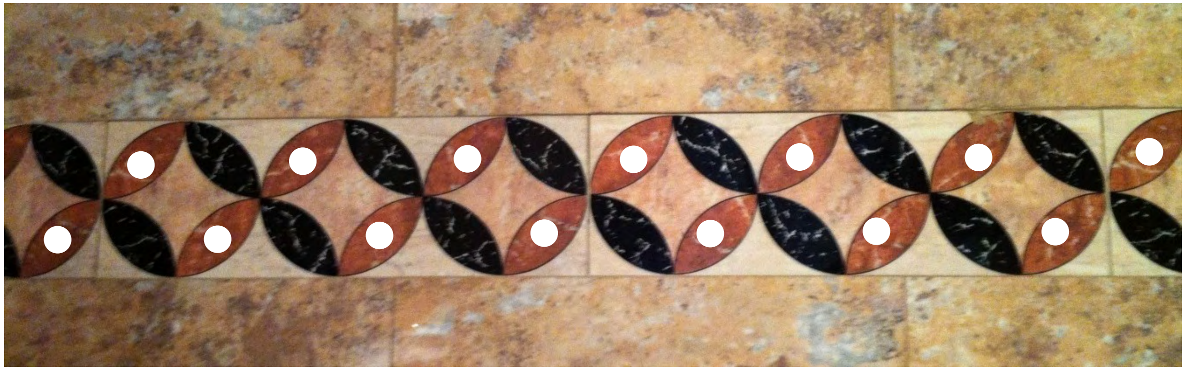
result of SC-HF calculation with site model

Hierarchical layout and design are possible.
Simple-12 microprocessor (Kogge & Niemier)



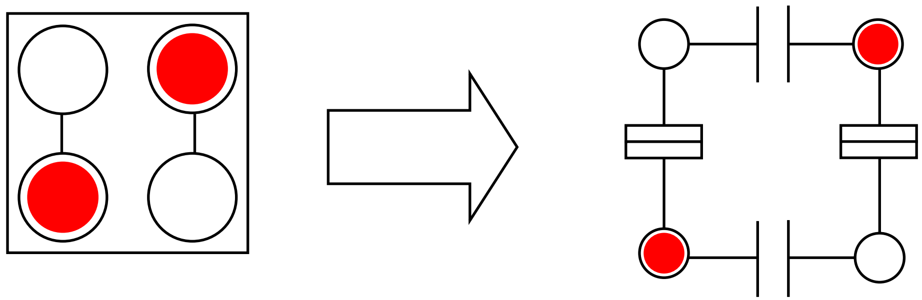


"1"

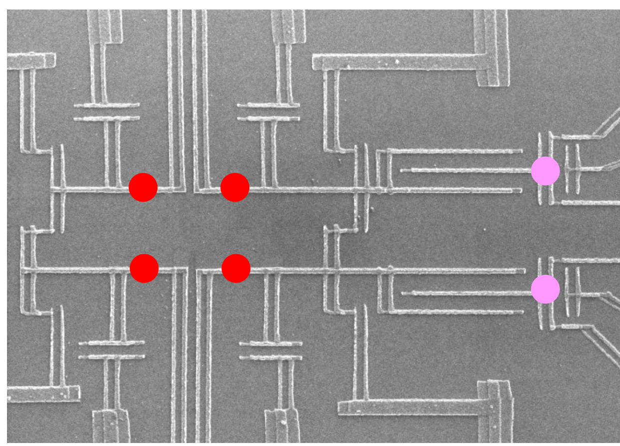


"0"

QCA devices and circuits exist



Metal-dot QCA implementation



Al/AlO_x on SiO_2

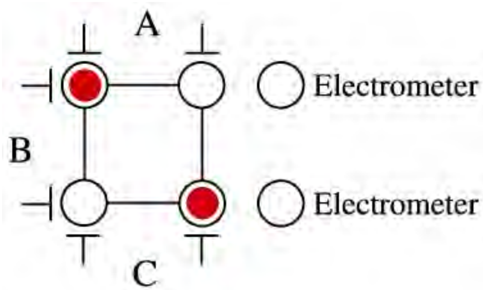
“dot” = metal island

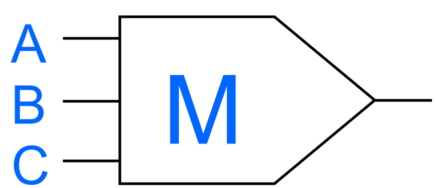
70-300 mK

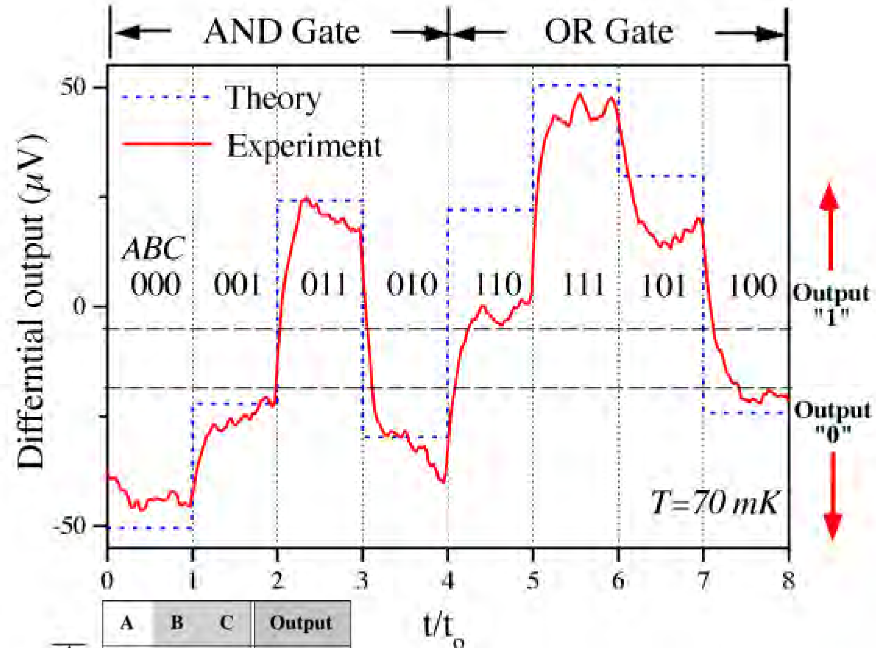
Greg Snider, Alexei Orlov, and Gary Bernstein

Metal-dot QCA cells and devices

- Majority Gate







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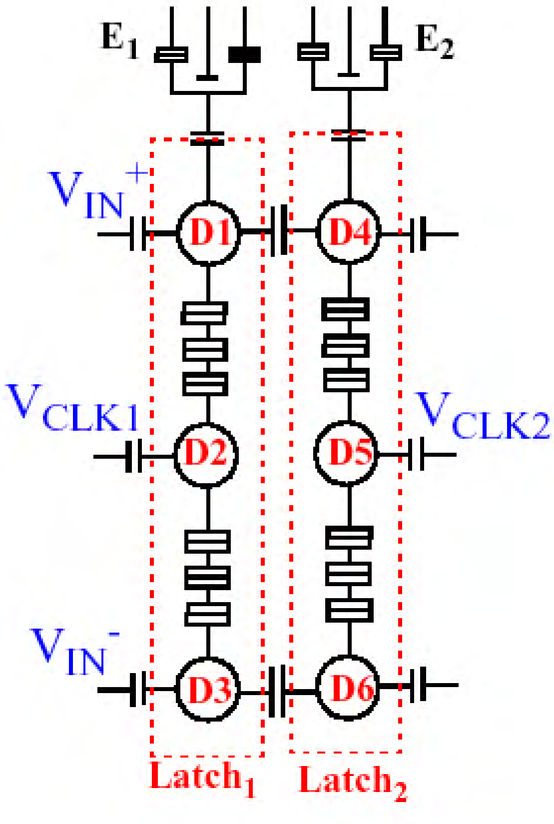
	1	1	1	1
	1	0	1	1
	1	0	0	0

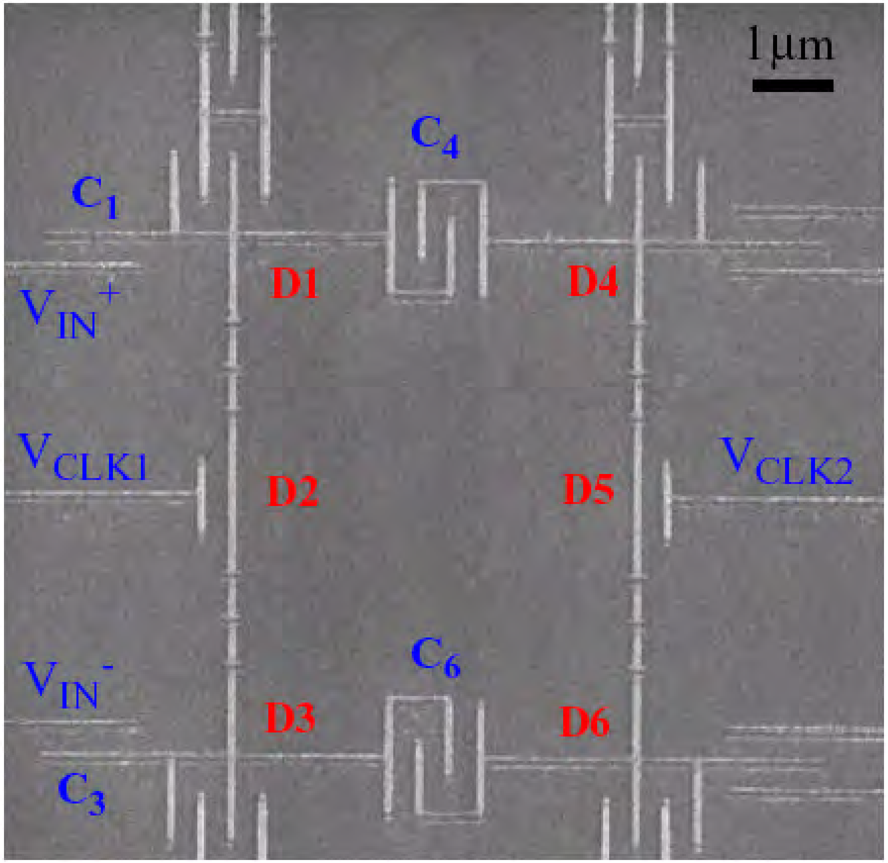
Amlani, A. Orlov, G. Toth, G. H. Bernstein, C. S. Lent, G. L. Snider, *Science* **284**, pp. 289-291 (1999).

QCA Shift Register

Schematic Diagram



SEM Micrograph

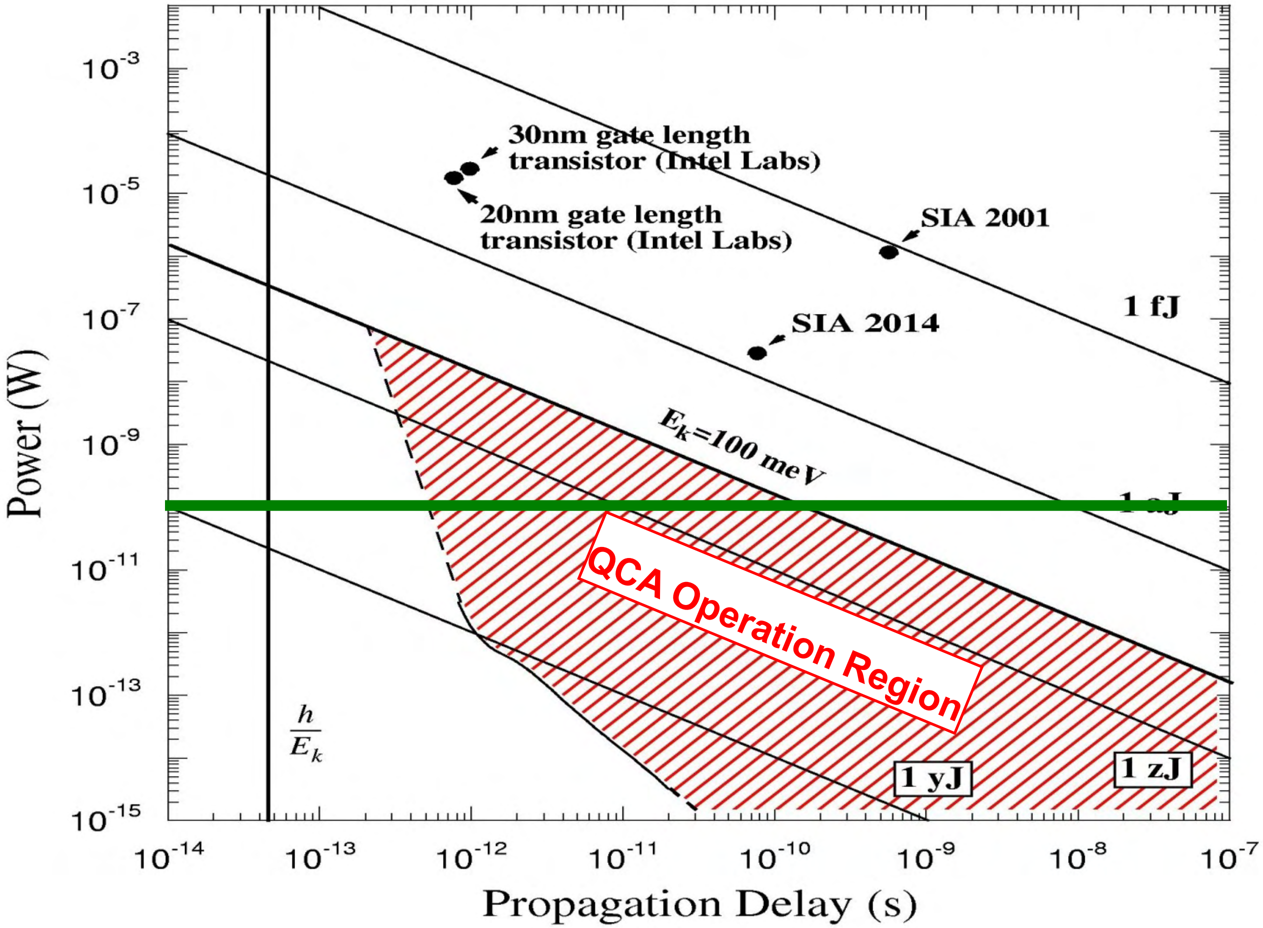


Metal-dot QCA devices exist

- Single electron analogue of molecular QCA
- Gates and circuits:
  - Wires
  - Shift registers
  - Inverters
  - AND, OR, Majority gates
  - Fan-out, Fan-in
  - Power gain demonstrated
  - Isolation of input from output

- Work underway to raise operating temperatures

QCA Power Dissipation



100 W/cm^2
@10^{12} devices/cm^2

QCA architectures might operate at densities of 10^{12} devices/cm^2 and 100GHz without melting the chip.

QCA implementations

- Semiconductor-dot QCA
- Metal-dot QCA
- Molecular QCA
- Magnetic QCA

GaAs-AlGaAs QCA cell

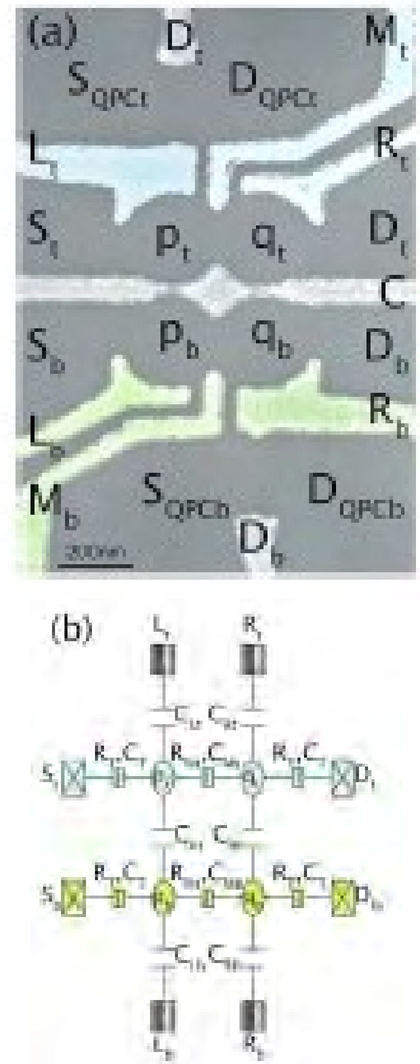
APPLIED PHYSICS LETTERS 91, 032102 (2007)

Demonstration of a quantum cellular automata cell in a GaAs/AlGaAs heterostructure

F. Perez-Martinez,[a] I. Farrer, D. Anderson, G. A. C. Jones, D. A. Ritchie, S. J. Chorley, and C. G. Smith
Cavendish Laboratory, University of Cambridge, J. J. Thomson Avenue, Cambridge CB3 0HE, United Kingdom

(Received 24 April 2007; accepted 21 June 2007; published online 17 July 2007)

The authors report on the experimental demonstration of a GaAs/AlGaAs-based quantum cellular automata cell fabricated using electron beam lithographically defined gates. These surface metallic gates form a pair of double quantum dots, as well as a pair of quantum point contacts (QPCs) that act as noninvasive voltage probes. Measurements at cryogenic temperatures show that an electron transfer in the input dots induces the relocation of a single electron in the output dots. Using the QPCs they were also able to determine the operating limits of the cell. © 2007 *American Institute of Physics*. [DOI: 10.1063/1.2759257]



- **Dots defined by top gates depleting 2DEG**
- **Direct measurement of cell switching**

Silicon P-dot QCA cell

APPLIED PHYSICS LETTERS **89**, 013503 (2006)

Demonstration of a silicon-based quantum cellular automata cell

M. Mitic,[a] M. C. Cassidy, K. D. Petersson,[b] R. P. Starrett, E. Gauja, R. Brenner, R. G. Clark, and A. S. Dzurak
Centre for Quantum Computer Technology, School of Electrical Engineering and School of Physics, The University of New South Wales, Sydney, New South Wales 2052, Australia

C. Yang and D. N. Jamieson
Centre for Quantum Computer Technology, School of Physics, University of Melbourne, Victoria 3010, Australia

(Received 8 March 2006; accepted 18 May 2006; published online 5 July 2006)

We report on the demonstration of a silicon-based quantum cellular automata (QCA) unit cell incorporating two pairs of metallically doped (n^+) phosphorus-implanted nanoscale dots, separated from source and drain reservoirs by nominally undoped tunnel barriers. Metallic cell control gates, together with Al–AlO_x single electron transistors for noninvasive cell-state readout, are located on the device surface and capacitively coupled to the buried QCA cell. Operation at subkelvin temperatures was demonstrated by switching of a single electron between output dots, induced by a driven single electron transfer in the input dots. The stability limits of the QCA cell operation were also determined. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2219128]

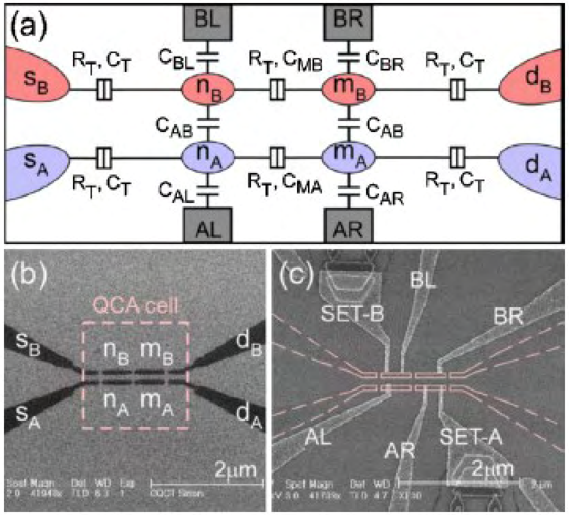


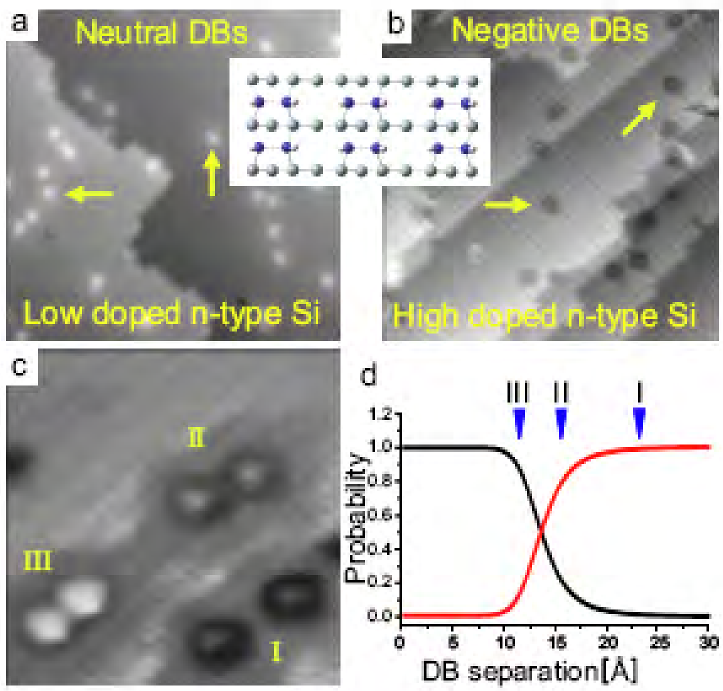
FIG. 1. (Color online) (a) Simplified circuit equivalent of the QCA cell, (b) SEM image of phosphorus-implanted n^+ regions (dark in image), and (c) SEM image of completed device. The buried n^+ dots and leads are marked using dashed lines.

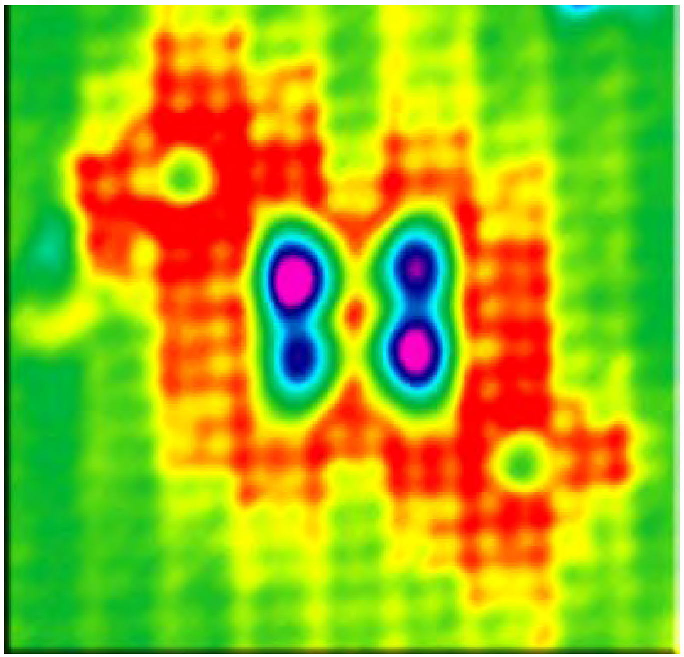
- **Dots defined by implanted phosphorus**
- **Single-donor creation foreseen**
- **Direct measurement of cell switching**

Single-atom quantum dots

Controlled Coupling and Occupation of Silicon Atomic Quantum Dots at Room Temperature

M. Baseer Haider[†,*] Jason L Pitters,[†] Gino A. DiLabio, Lucian Livadaru,[*] Josh Y Mutus,[*] and Robert A. Wolkow[*]
National Institute for Nanotechnology, National Research Council of Canada
11421 Saskatchewan Drive, Edmonton, Alberta T6G 2M9, Canada[‡]
(Dated: October 11, 2008)





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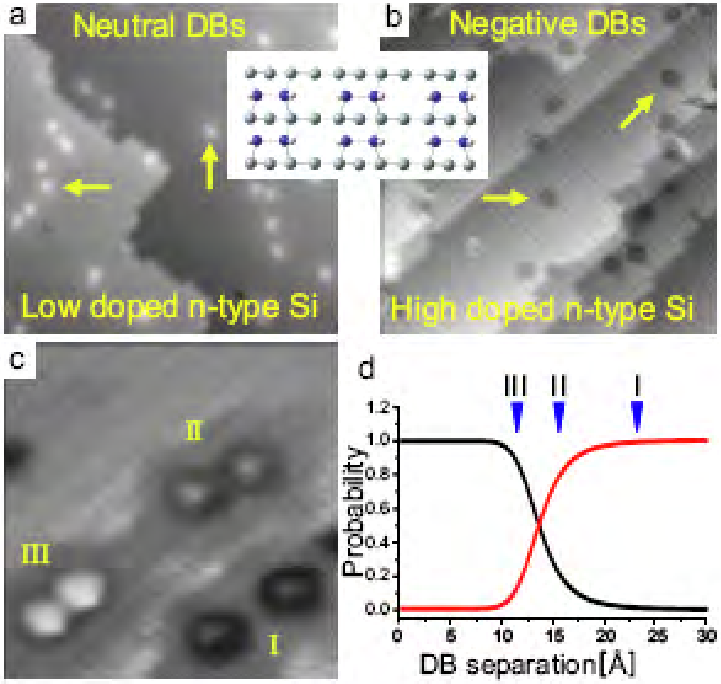
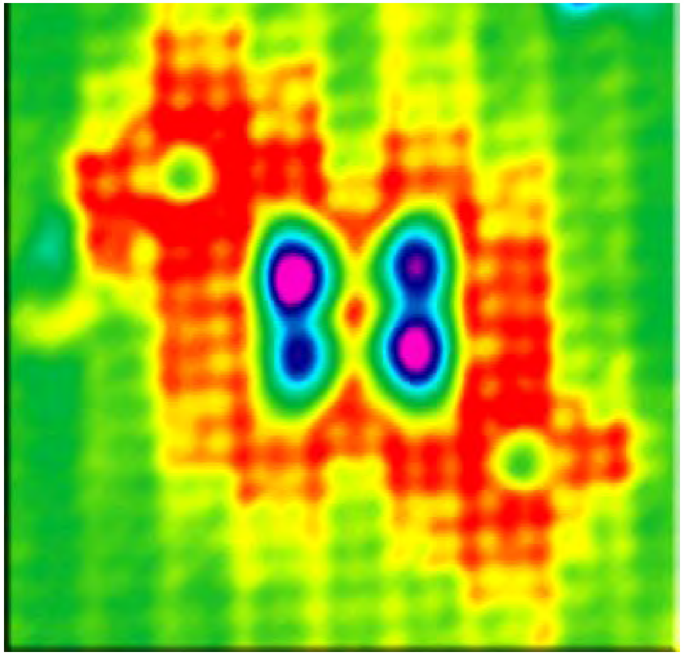




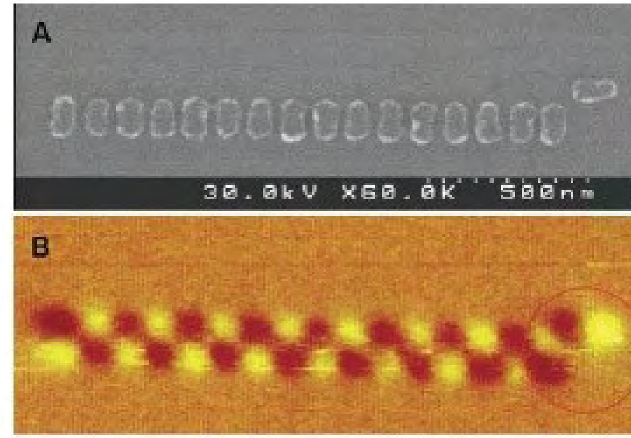
Magnetic QCA

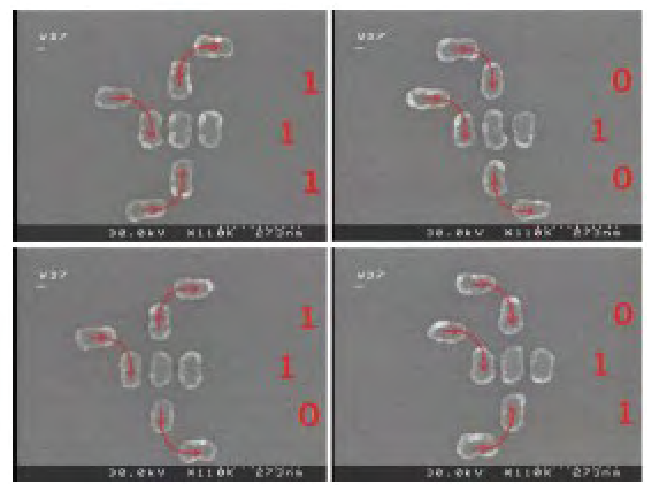
SCIENCE VOL 311 13 JANUARY 2006

Majority Logic Gate for Magnetic Quantum-Dot Cellular Automata

A. Imre,[1]* G. Csaba,[2] L. Ji,[1] A. Orlov,[1] G. H. Bernstein,[1] W. Porod[1]

We describe the operation of, and demonstrate logic functionality in, networks of physically coupled, nanometer-scale magnets designed for digital computation in magnetic quantum-dot cellular automata (MQCA) systems. MQCA offer low power dissipation and high integration density of functional elements and operate at room temperature. The basic MQCA logic gate, that is, the three-input majority logic gate, is demonstrated.

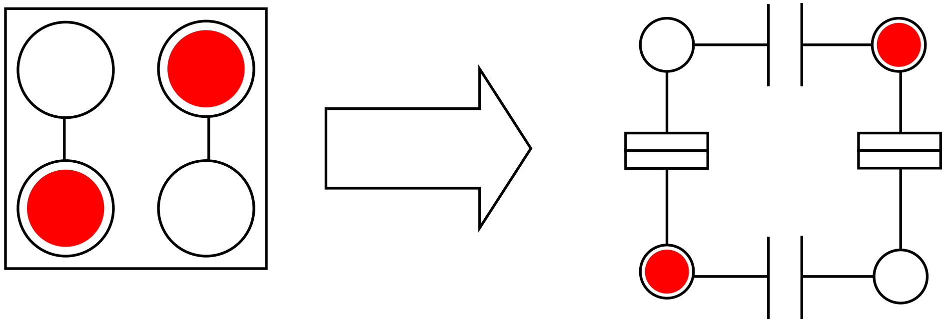


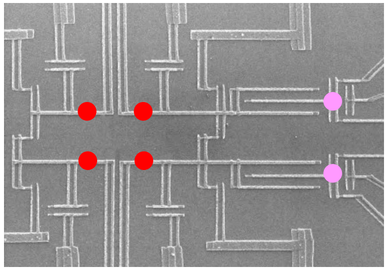


- **Dots defined by magnetic domains**
- **Room temperature operation**

From metal-dot to molecular QCA

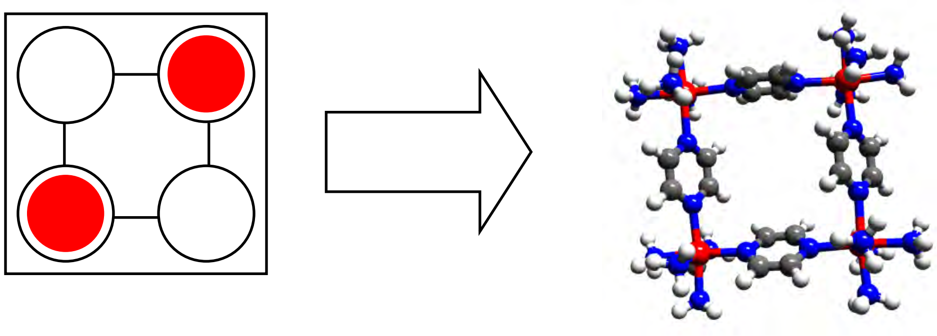
Metal tunnel junctions





"dot" = metal island

70 mK



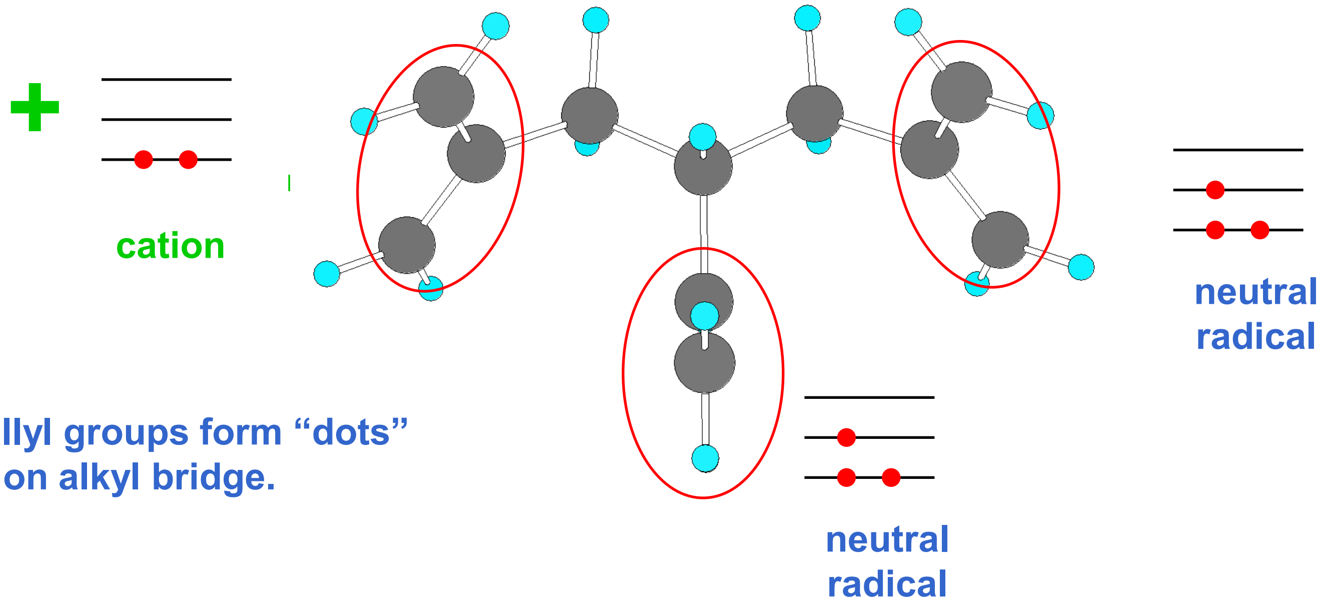
"dot" = redox center

Mixed valence compounds

room temperature+

Key strategy: use *nonbonding* orbitals (π or d) to act as dots.

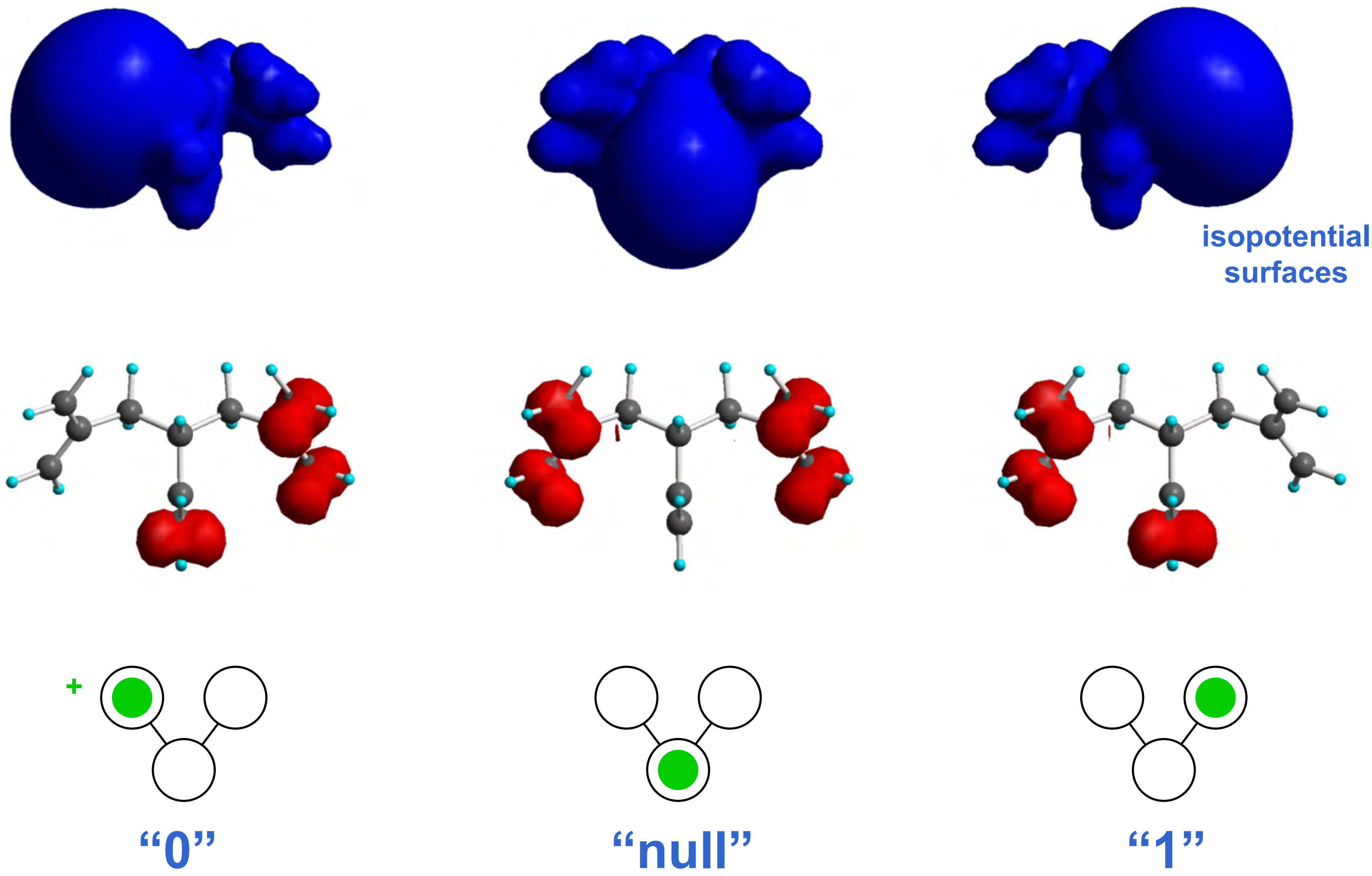
Molecular 3-dot cell



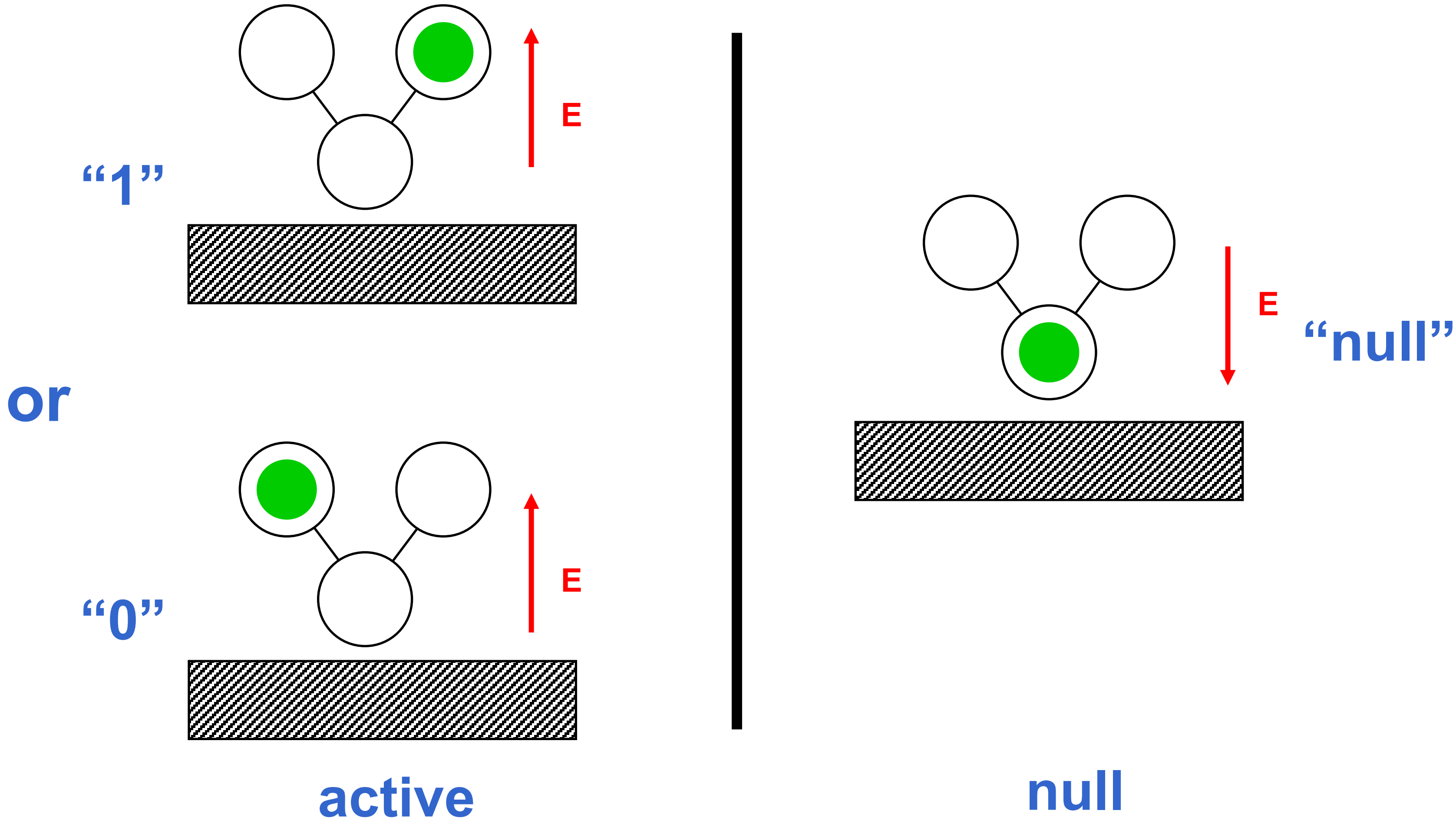
Three allyl groups form “dots”
on alkyl bridge.

For the molecular cation, a hole occupies one of three dots.

Charge configuration represents bit

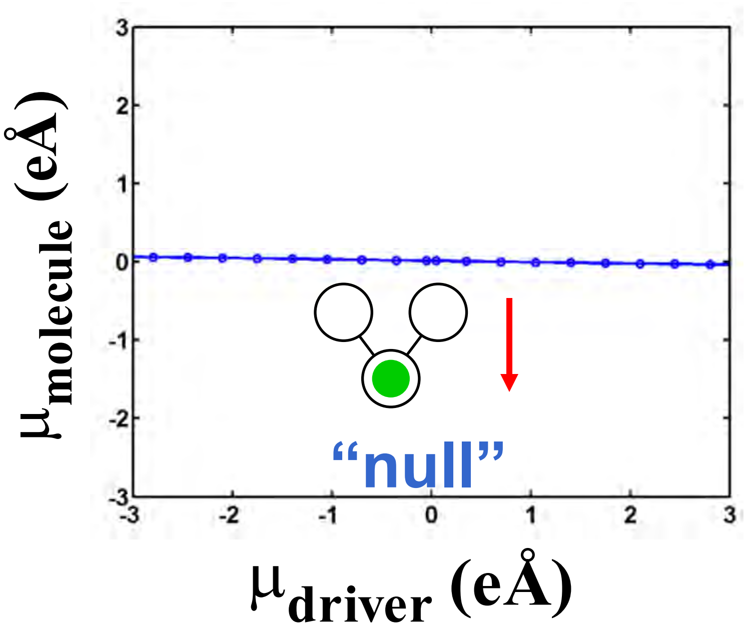


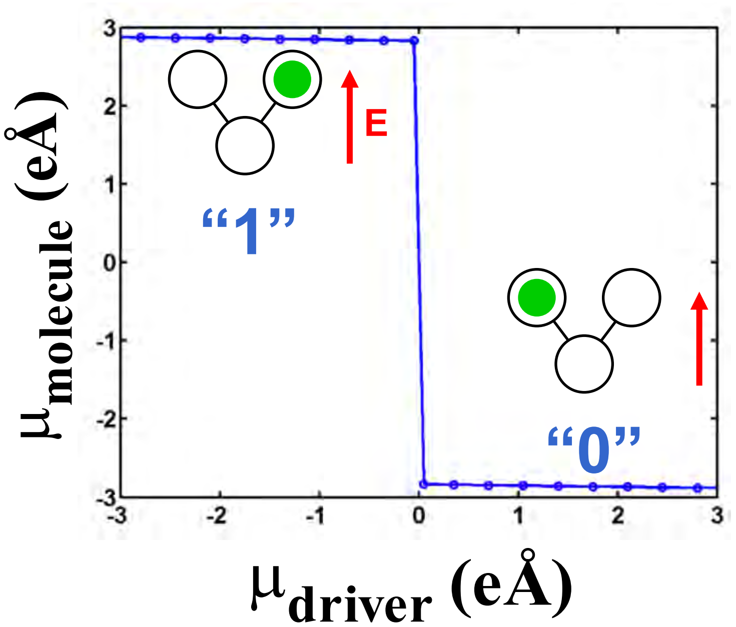
Clocking field



Use local electric field to switch molecule between active and null states.

Clocking field alters response function

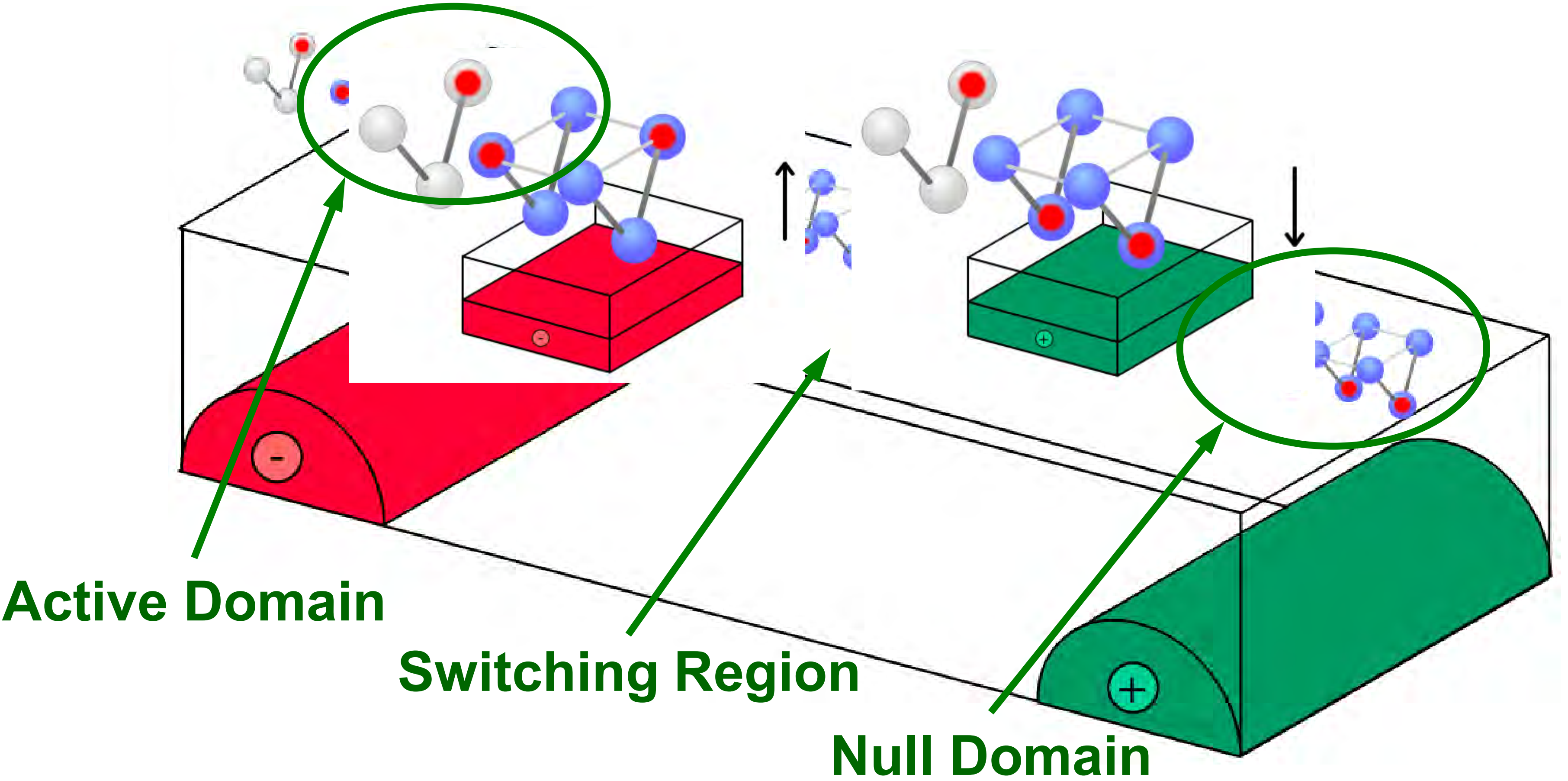




- Clocking field negative
- Positive charge in bottom dot
- Cell is inactive – no response to input

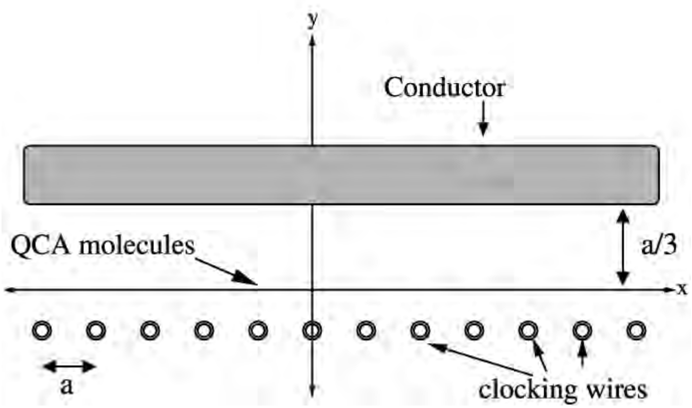
- Clocking field positive (or zero)
- Positive charge in top dots
- Cell is active – nonlinear response to input

Clocked Molecular QCA

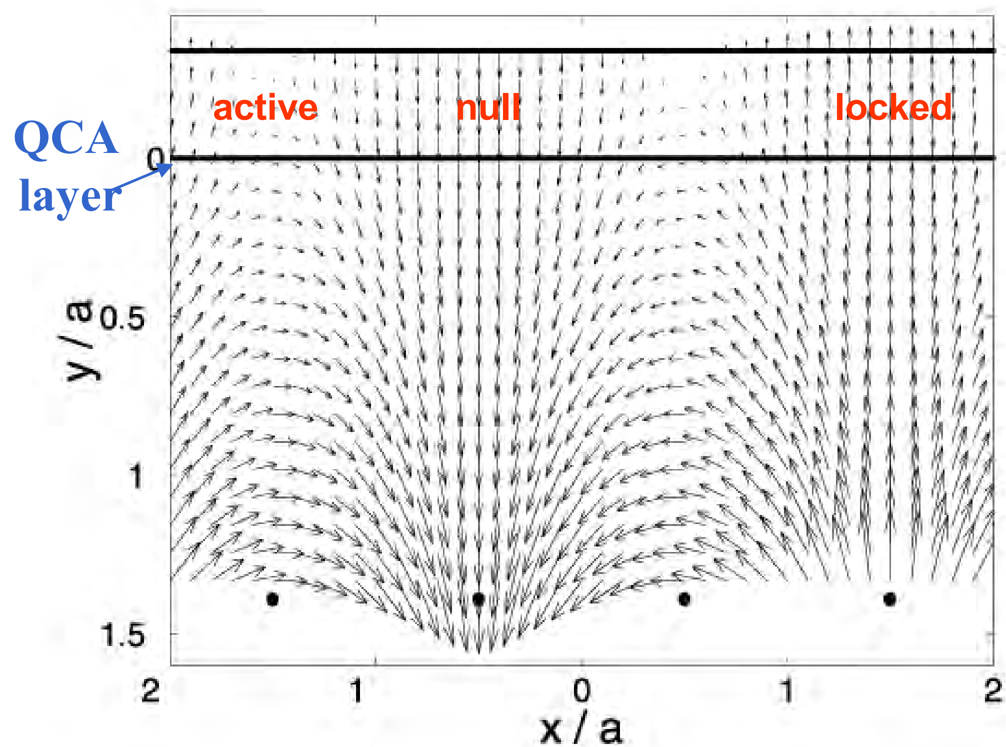


No current leads. No need to contact individual molecules.

Molecular clocking



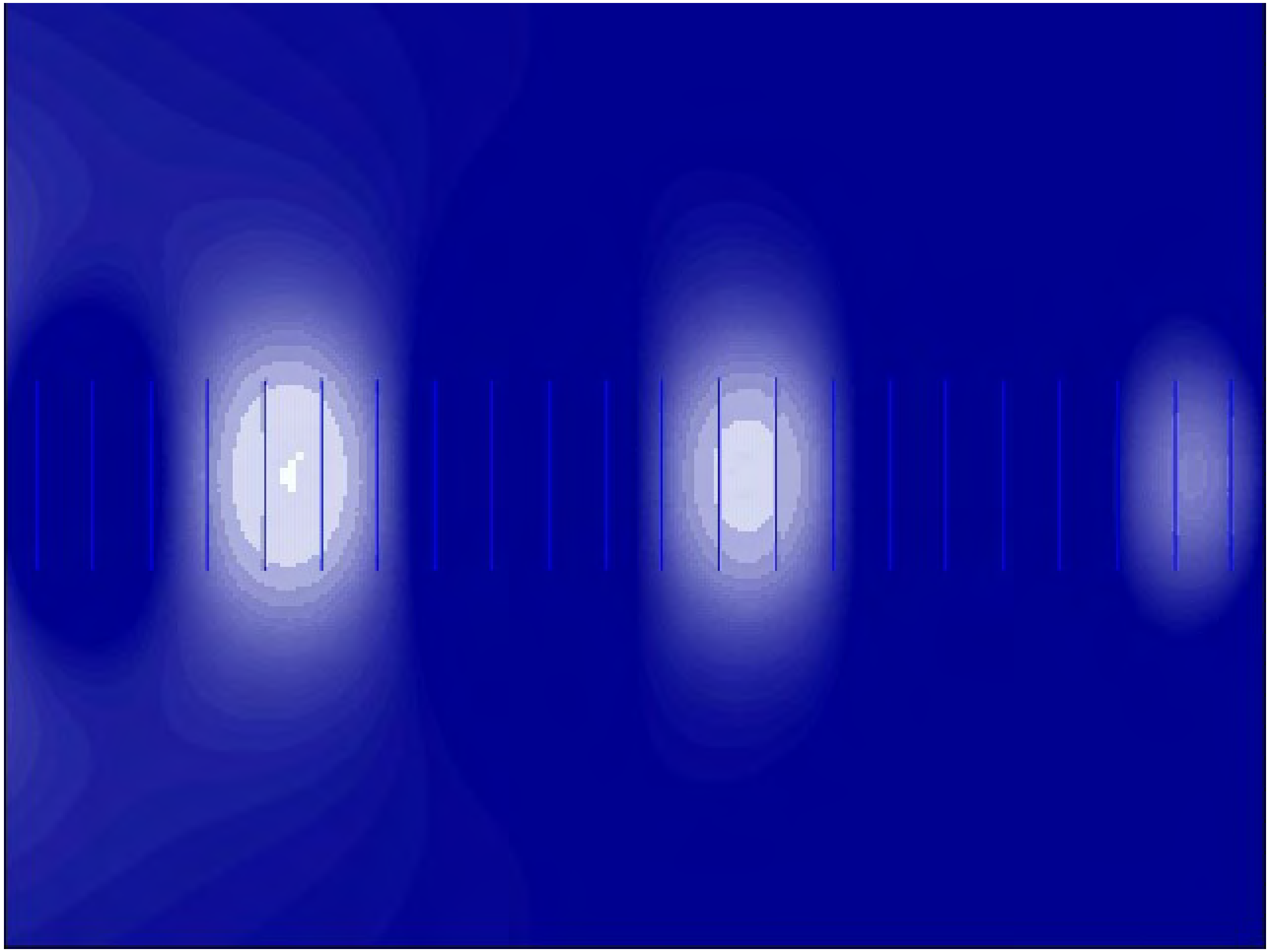
Hennessey and Lent, JVST (2001)



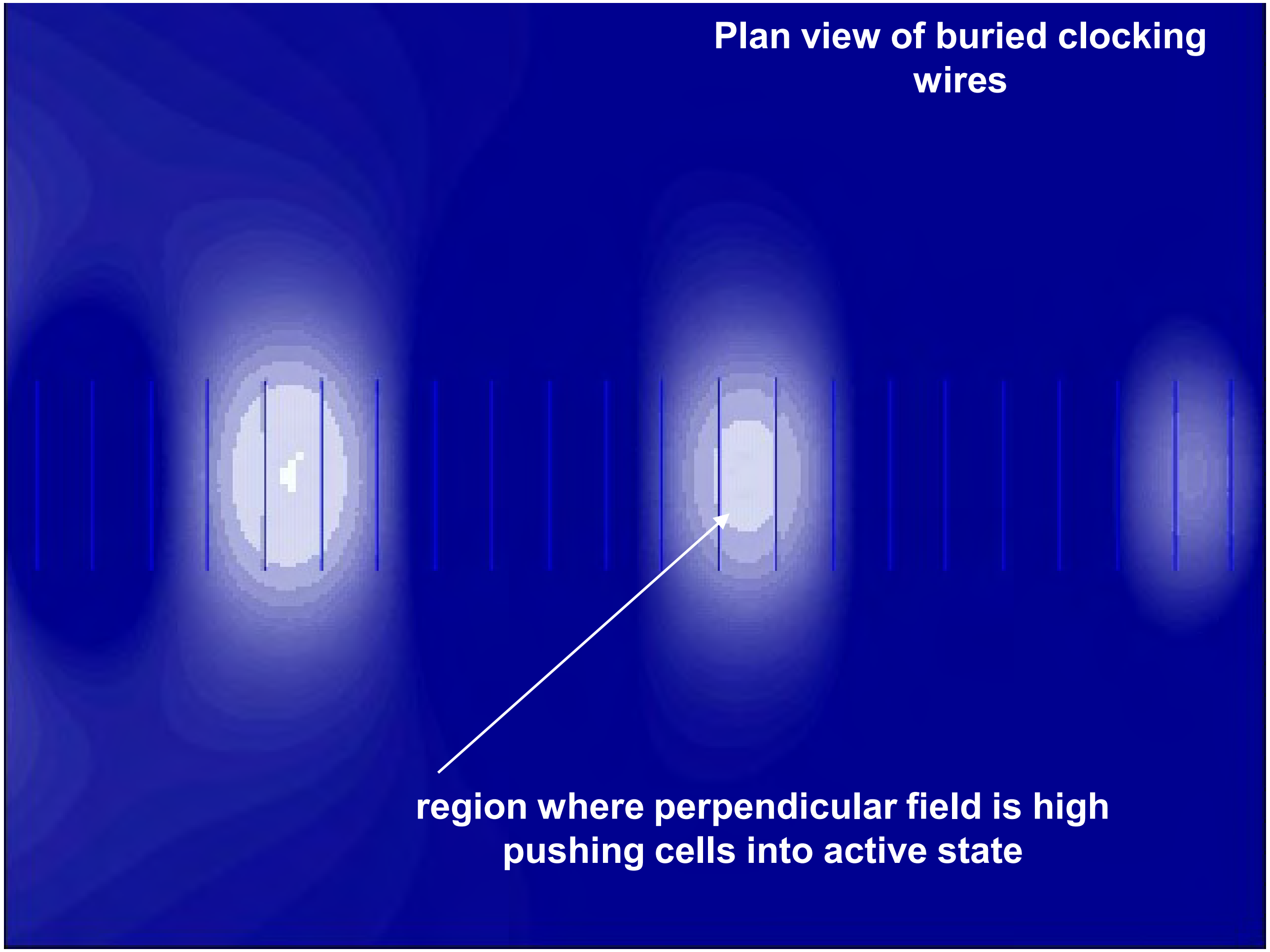
Clocking field is provided by buried wire electrodes (CMOS controlled).

Wire sizes can be 10-100 times larger than molecules.

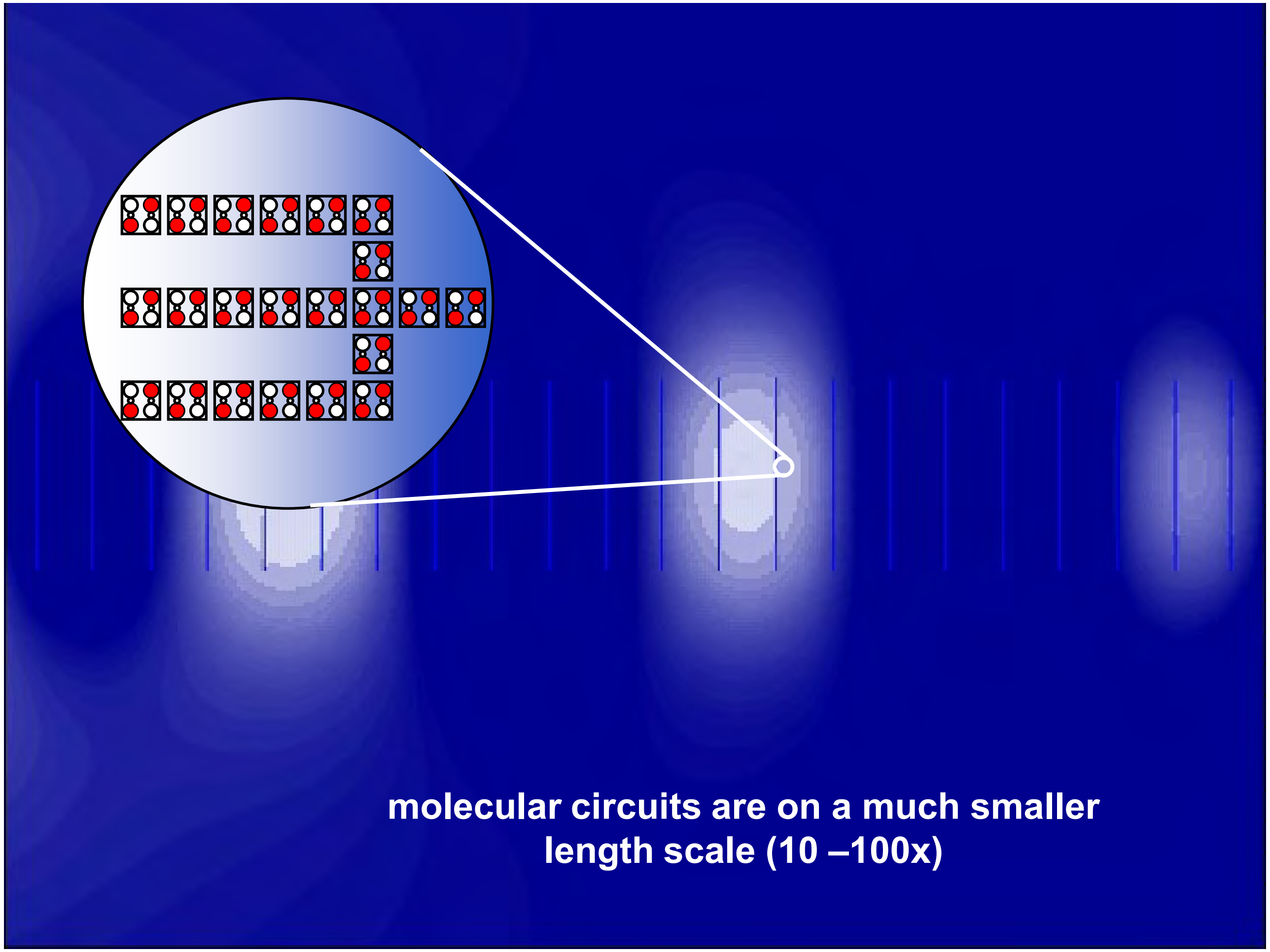
Clocking field



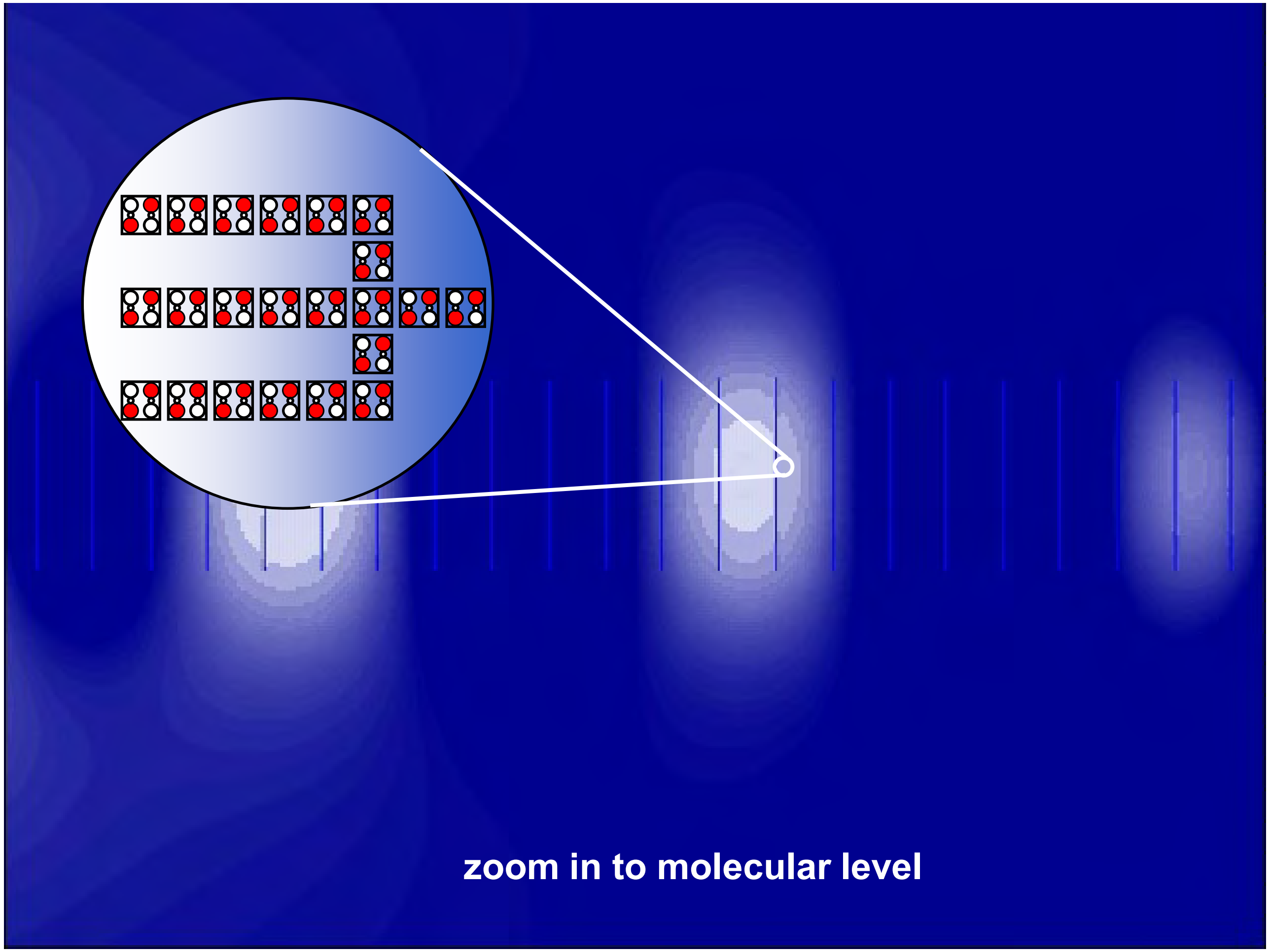
Molecular circuits and clocking wires



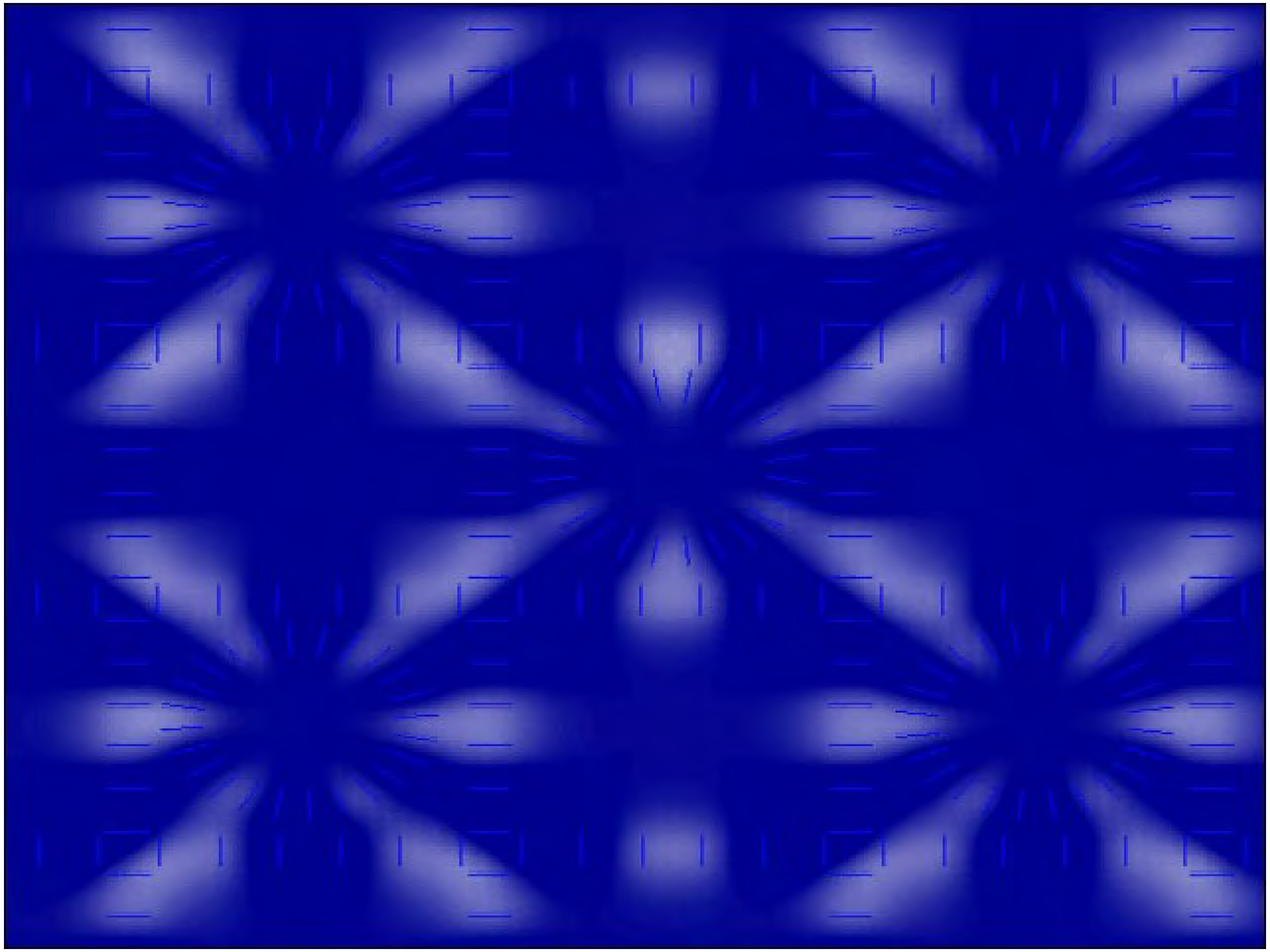
Molecular circuits and clocking wires



Molecular circuits and clocking wires

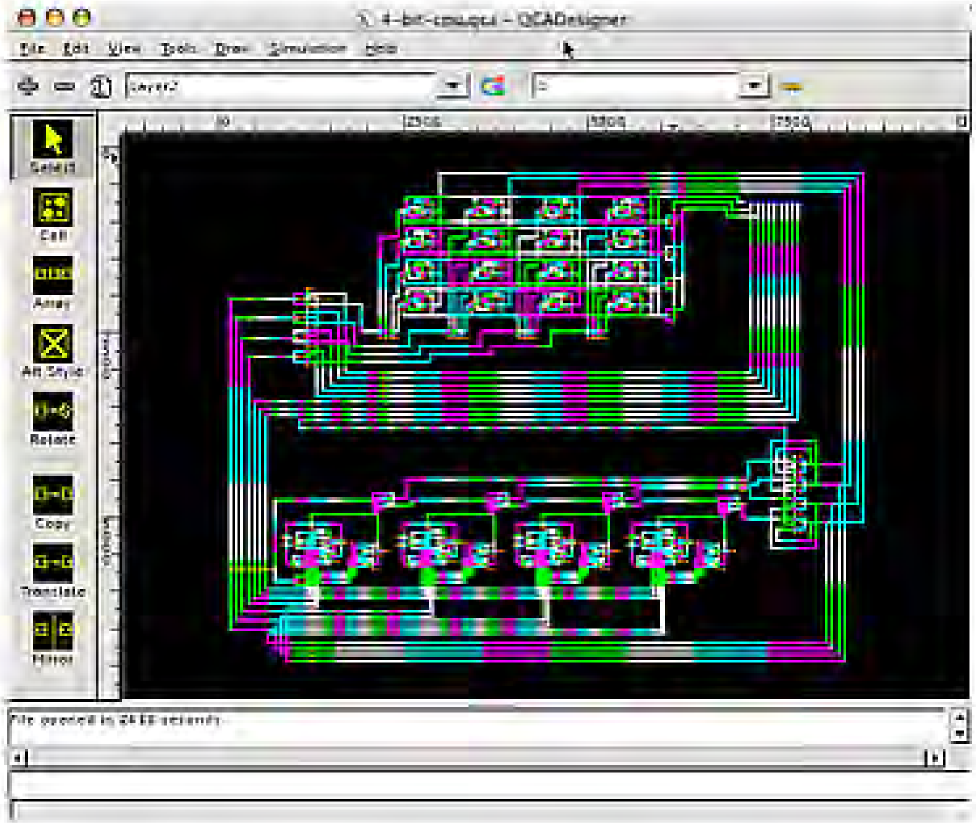


Universal floorplan



Peter Kogge

QCA design tools



QCADesigner

Konrad Walus
U. British Columbia

QCADesigner screenshot showing a simple 4-bit processor layout.

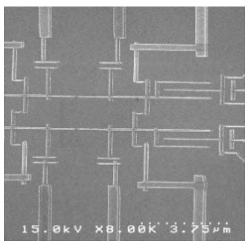
Design tools are starting to enable new systems ideas.

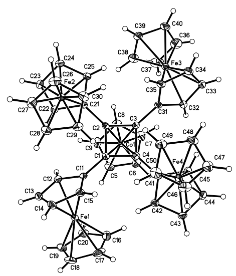
System + Application Architectures

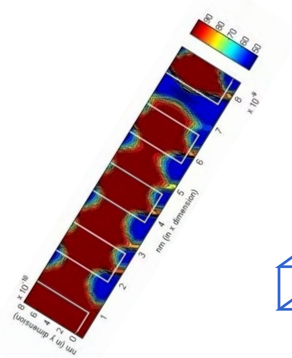
Mike Niemier

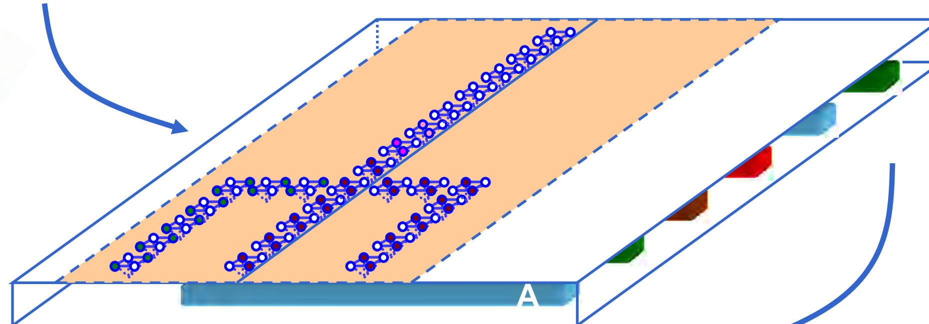
Grounded in device physics & simulation

Incorporate clock driven dataflow



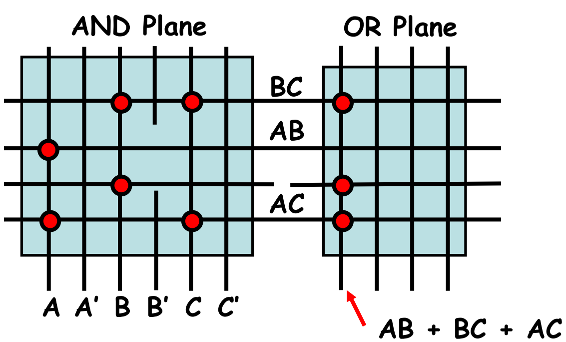




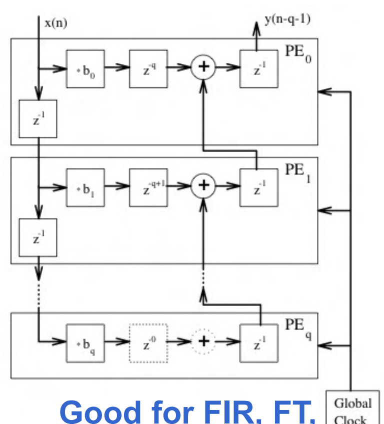


Device architecture maps well to many system architectures…

Reconfigurable

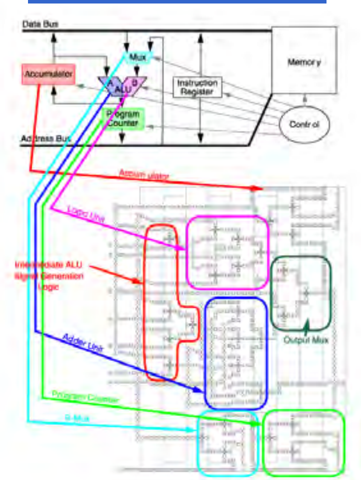


Systolic



Good for FIR, FT, Matrix multiply, graph algorithms, etc.

General Purpose

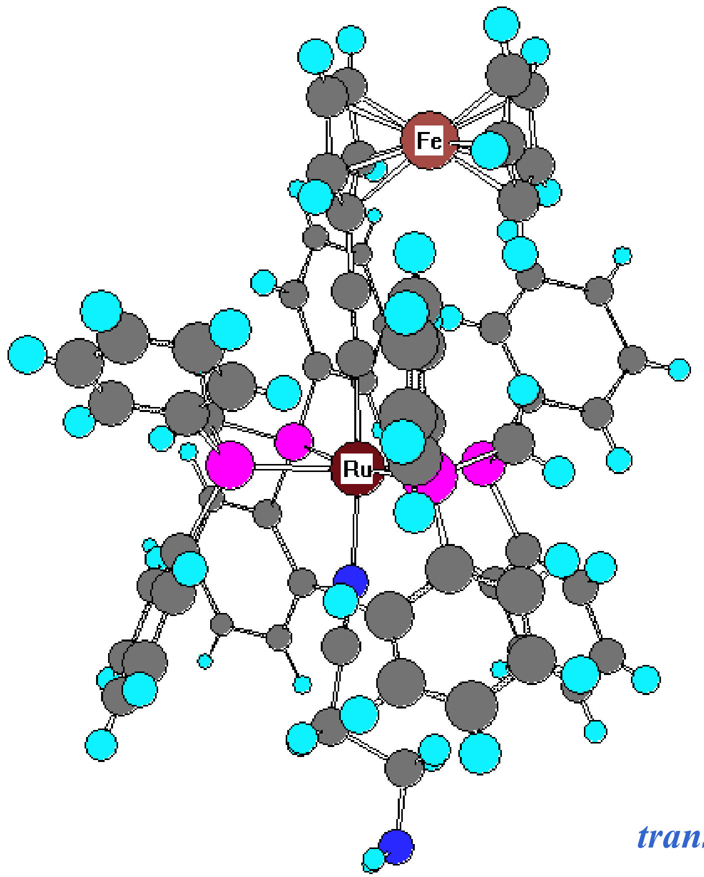


QCA molecular systems

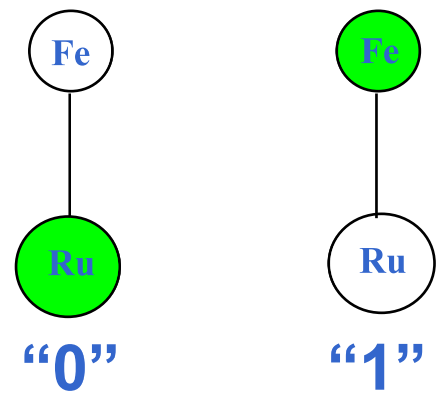
- ✓ • Diallyl double-dot (Aviram)
- ✓ • Clocked tri-allyl
- Ru-Fc double dot (Fehlner)
- Ru-Ru double dot (Fehlner)
- Fc 4-dot system (Fehlner)

synthesized

Experiments on molecular double-dot



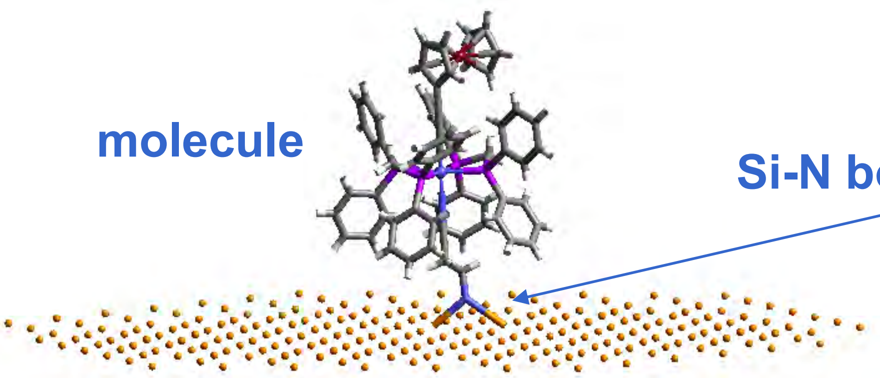
Thomas Fehlner
(Notre Dame chemistry group)

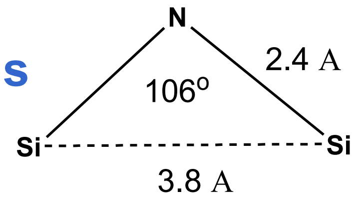


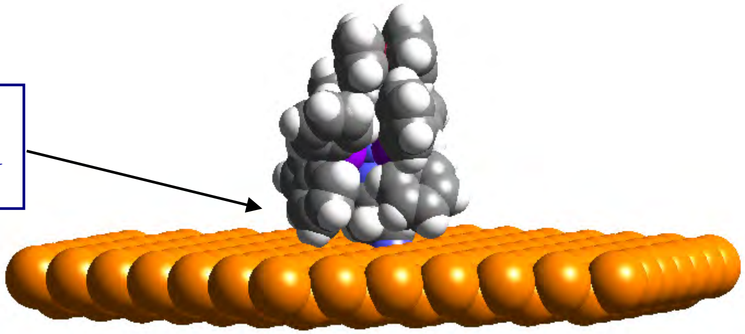
trans-Ru-$(dppm)_2(C{\equiv}CFc)(NCCH_2CH_2NH_2)$ dication

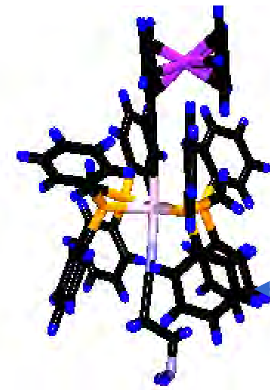
Fe group and Ru group act as two *unequal* quantum dots.

Surface attachment and orientation







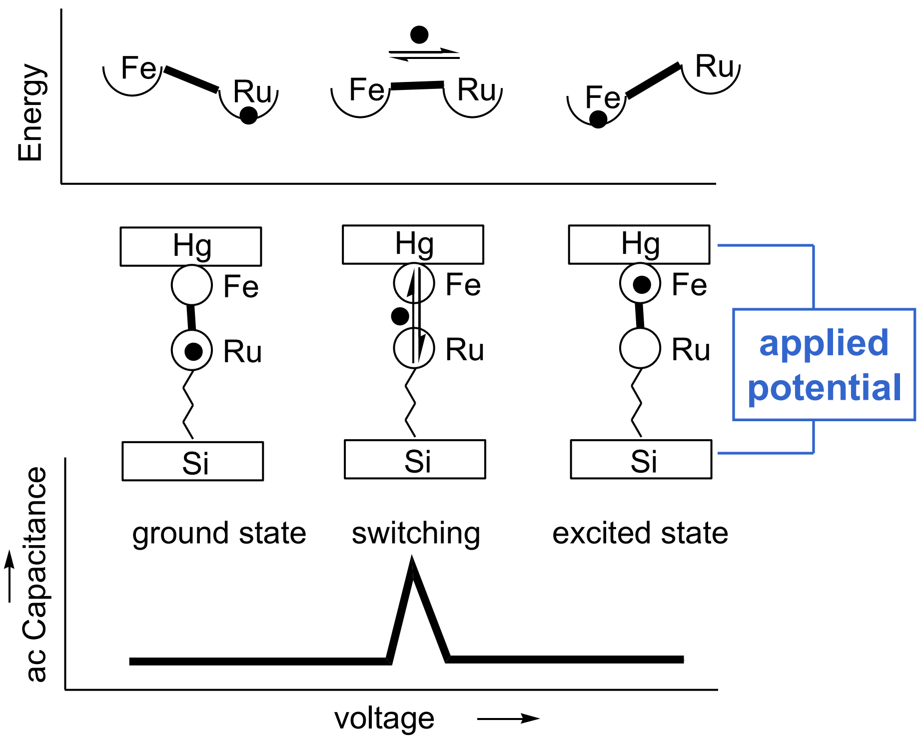


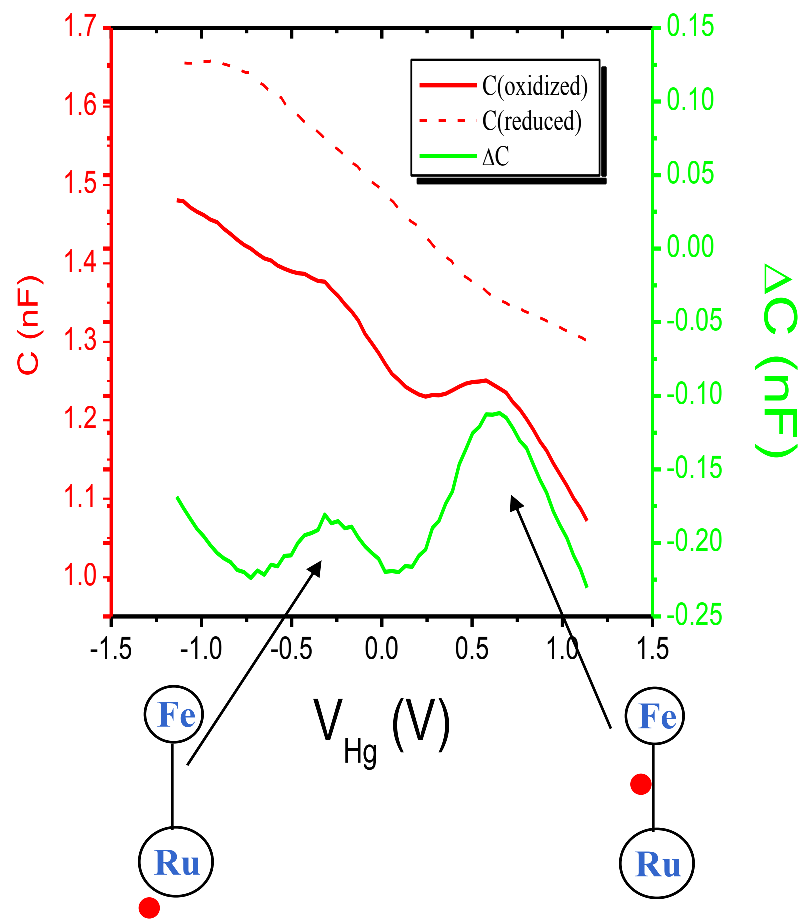
Molecule is covalent bonded to Si and oriented vertically by "struts."

Measurement of molecular bistability

layer of molecules

Applied field *equalizes* the energy of the two dots

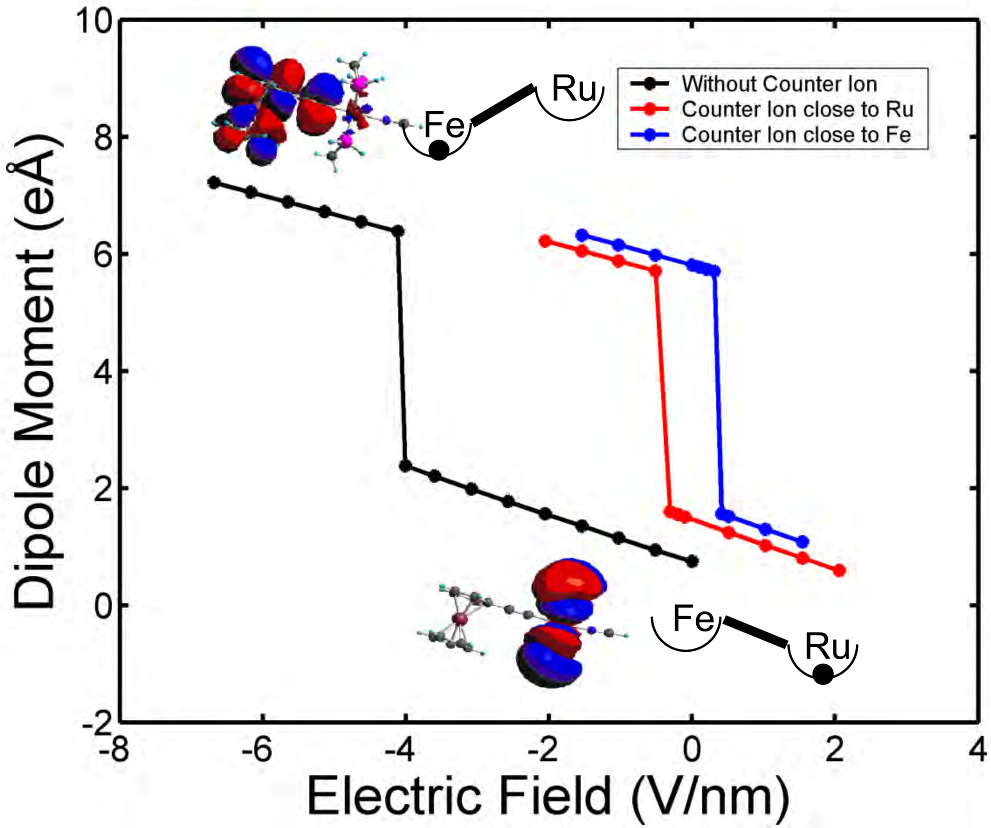




When equalized, capacitance peaks.

2 counterion charge configurations on surface

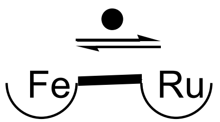
Switching by an applied field



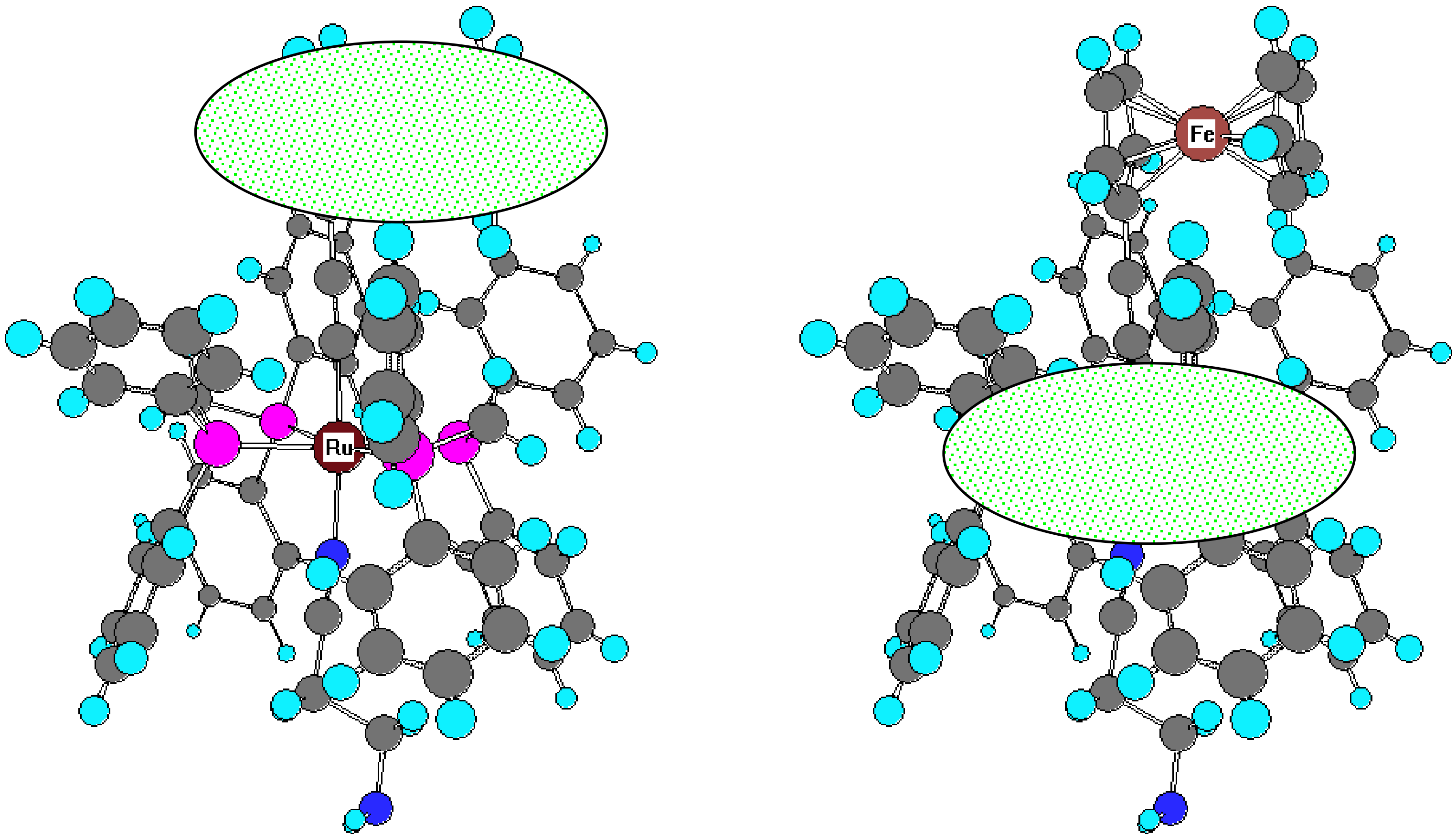
Gaussian

Mobile electron driven by electric field, the effect of counterions shift the response function.

Click-clack correspond to:

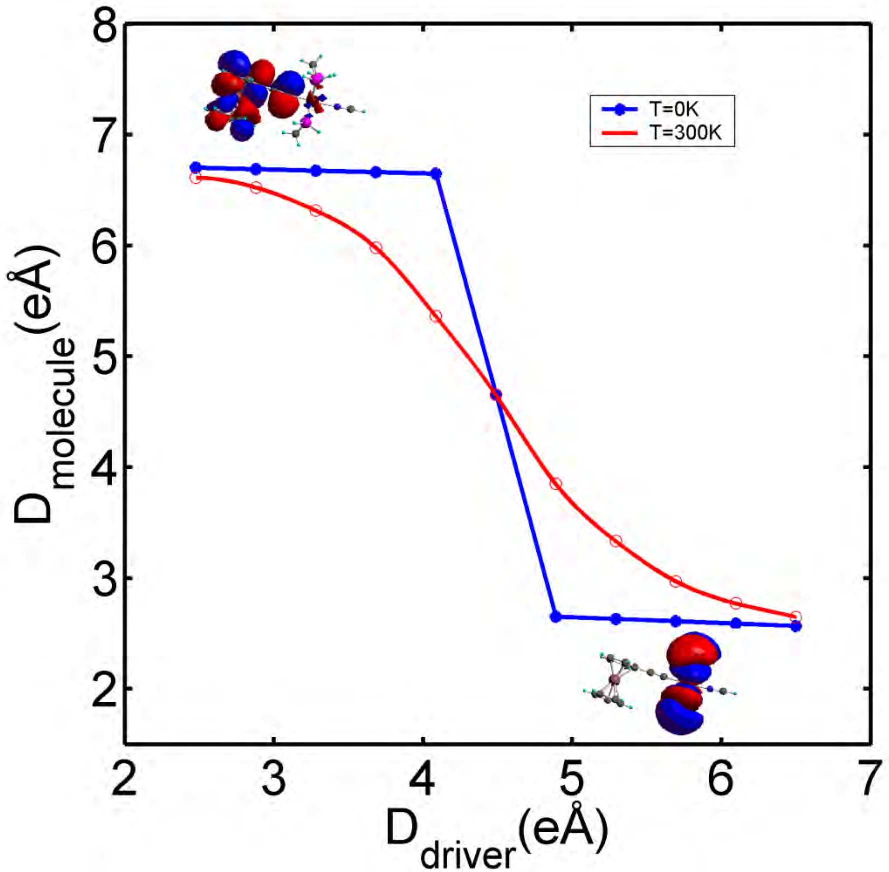


Molecule-molecule interaction



Can one molecule switch another molecule?

Switching by a neighboring molecule



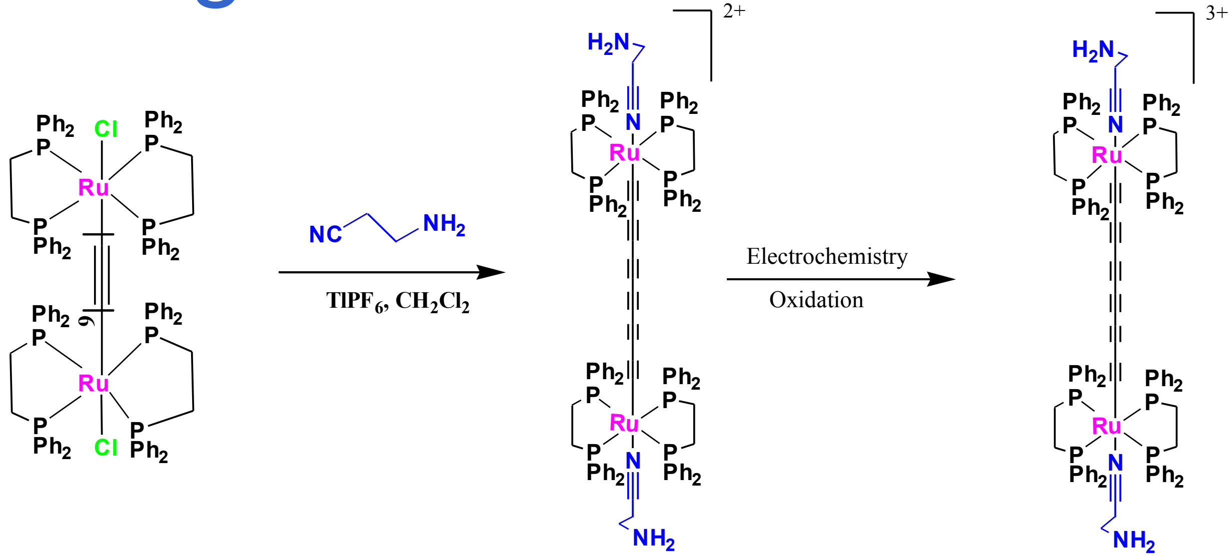
The distance between Neighboring molecules: **1 nm**

External electric field: **1.2 V/nm**

All counterions attach to the substrate

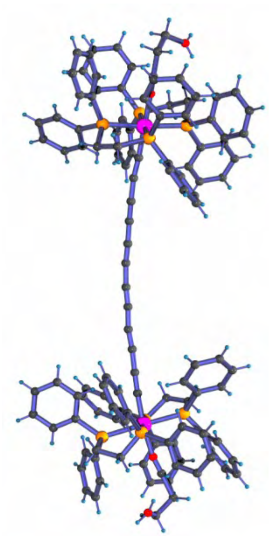
One molecule *can* switch a neighboring molecule.

Longer double-dot molecule

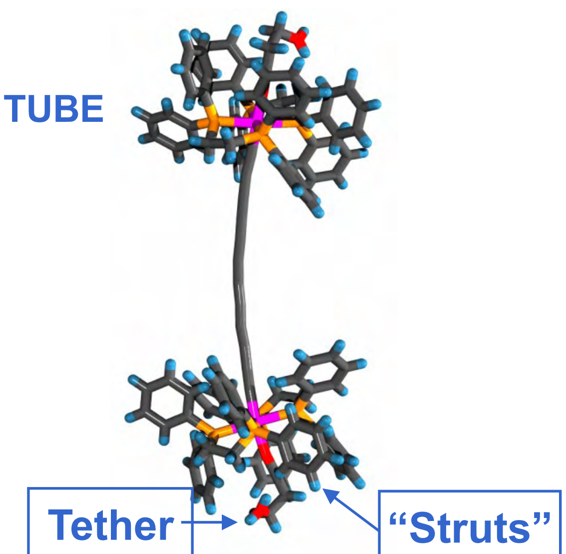


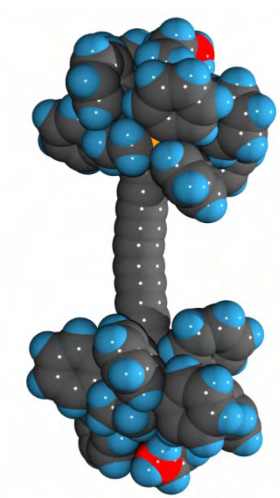
Hua & Fehlner

BALL & STICK



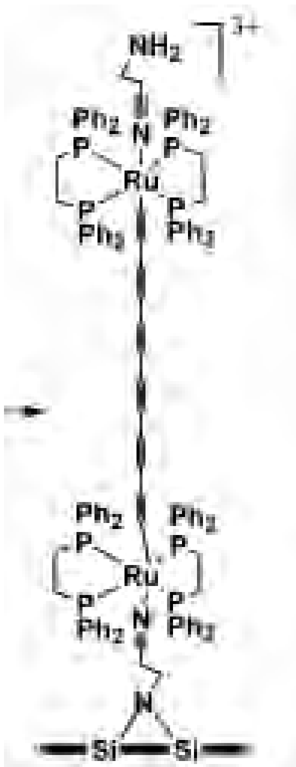
TUBE



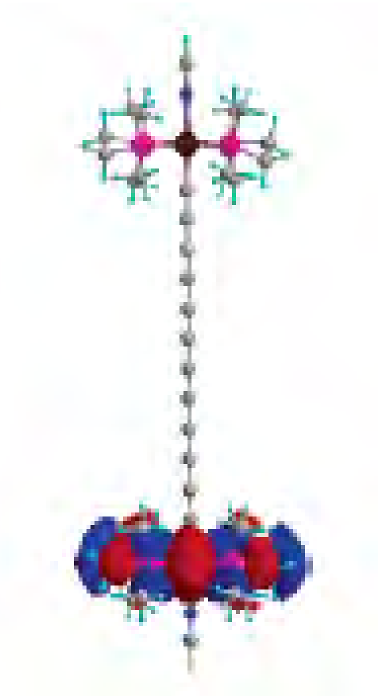


SPACE FILLING

Longer molecular double-dot

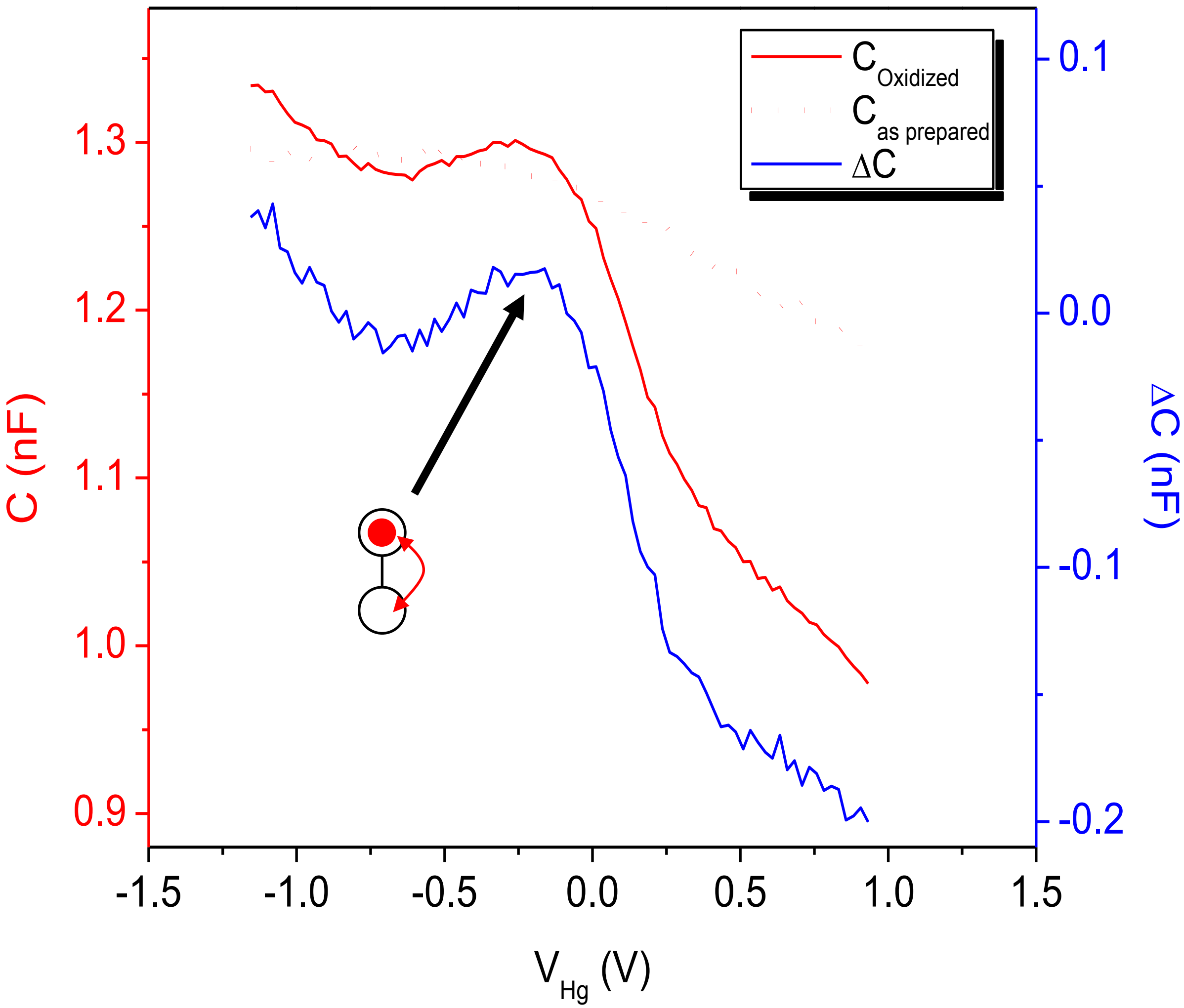


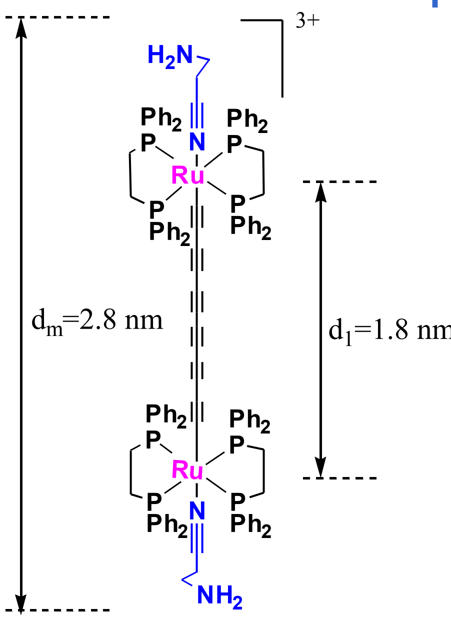
Isopotential surface



HOMO orbital

Double-dot click-clack





Hua & Fehlner

Square 4-dot QCA molecules

J|A|C|S
COMMUNICATIONS

Published on Web 06/03/2003

Building Blocks for the Molecular Expression of Quantum Cellular Automata. Isolation and Characterization of a Covalently Bonded Square Array of Two Ferrocenium and Two Ferrocene Complexes

Jieying Jiao,† Gary J. Long,*‡ Fernande Grandjean,§ Alicia M. Beatty,† and Thomas P. Fehlner*,†

Department of Chemistry & Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556-5670, Department of Chemistry, University of Missouri—Rolla, Rolla, Missouri 65409-0010, and Department of Physics, B5, University of Liege, B-4000 Sart-Tilman, Belgium

Received March 10, 2003; E-mail: fehner.1@nd.edu

The utilization of molecules as components of electronic circuits has caught the imagination of many.[1] The temptation to look for molecular mimics of existing electronic components is strong; however, molecules are exceedingly poor charge conductors and resistive heating rules out high device densities—the primary justification of the approach. On the other hand, molecules are excellent charge containers and a novel paradigm, quantum cellular automata (QCA), which is based on field-coupled charge containers, has been proven theoretically as well as operationally at low temperature using 50 nm quantum dots.[2−4] Systems based on 2 nm dots are expected to operate at room temperature, hence, our interest in developing molecular expressions of the QCA paradigm.[5]

The smallest building block of QCA wires consists of two dots containing a single mobile electron. At the molecular level this building block is a mixed-valence complex about which much is known.[6−8] A more versatile building block for constructing QCA circuits is a square of four electronically coupled dots containing two mobile electrons. Although molecular squares containing redox active metal centers have been described[9−14] and mixed-valence complexes up to nuclearity three have been thoroughly analyzed,[6,15] there is no example of an isolated four-metal, mixed-valence complex containing two mobile electrons in a square geometry. The independent existence and compatible electronic properties of such a species are of fundamental importance to the realization of the QCA paradigm. Here we report the full characterization of a symmetrical square containing two ferrocene and two ferrocenium moieties possessing measured properties that make it suitable for use as a component for charge-coupled QCA circuits.

The basic requirements to be met by a molecular QCA cell are dots consisting of metal complexes possessing two stable redox states, a planar array of four such complexes with 4-fold symmetry,

Figure 1. Molecular structure of [1][PF$_6$]. Fe−Fe edge distance 5.980 Å. The η^5-C_5H_5 ring bound to the Co atom (green) is not shown for clarity.

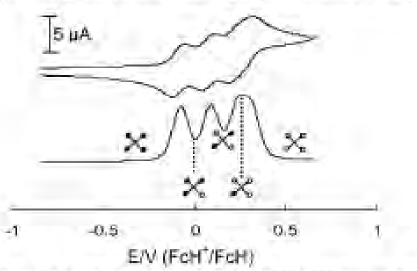
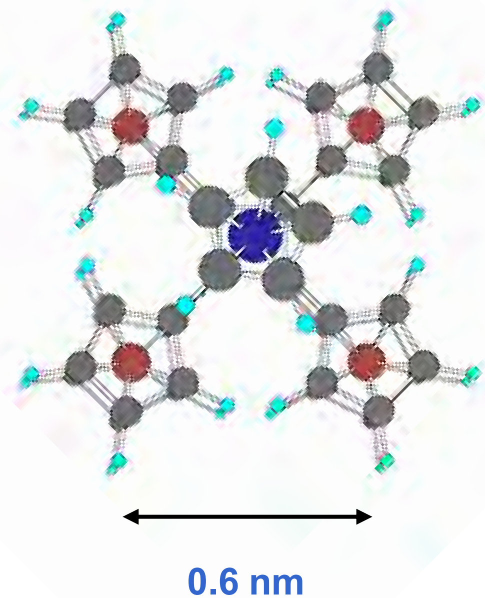
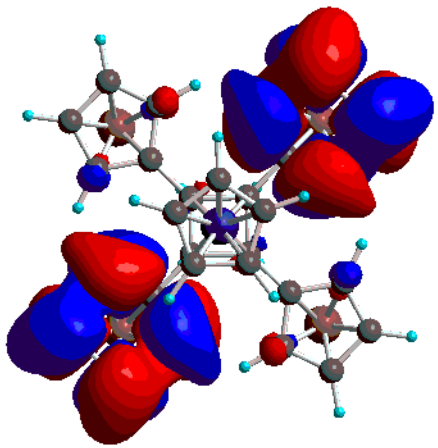


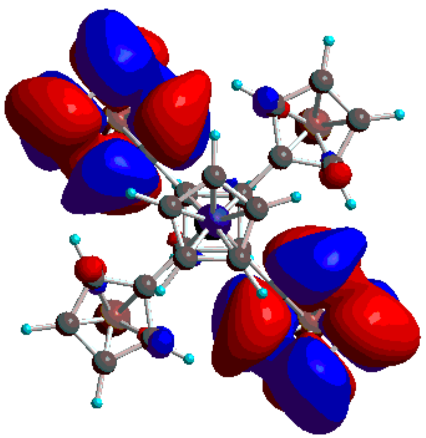
Figure 2. Cyclic and square wave voltammetry of 1 at 100 mV/s on a Pt electrode in CH_2Cl_2/CH_3CN mixed solvent, TBA[PF$_6$] electrolyte, and Pt wire reference electrode ($E_{1/2}$(FcH$^+$/FcH) = 0.344 V). The solid and open dots in the diagrams represent Fe(II) and Fe(III), respectively.



Bistable configurations



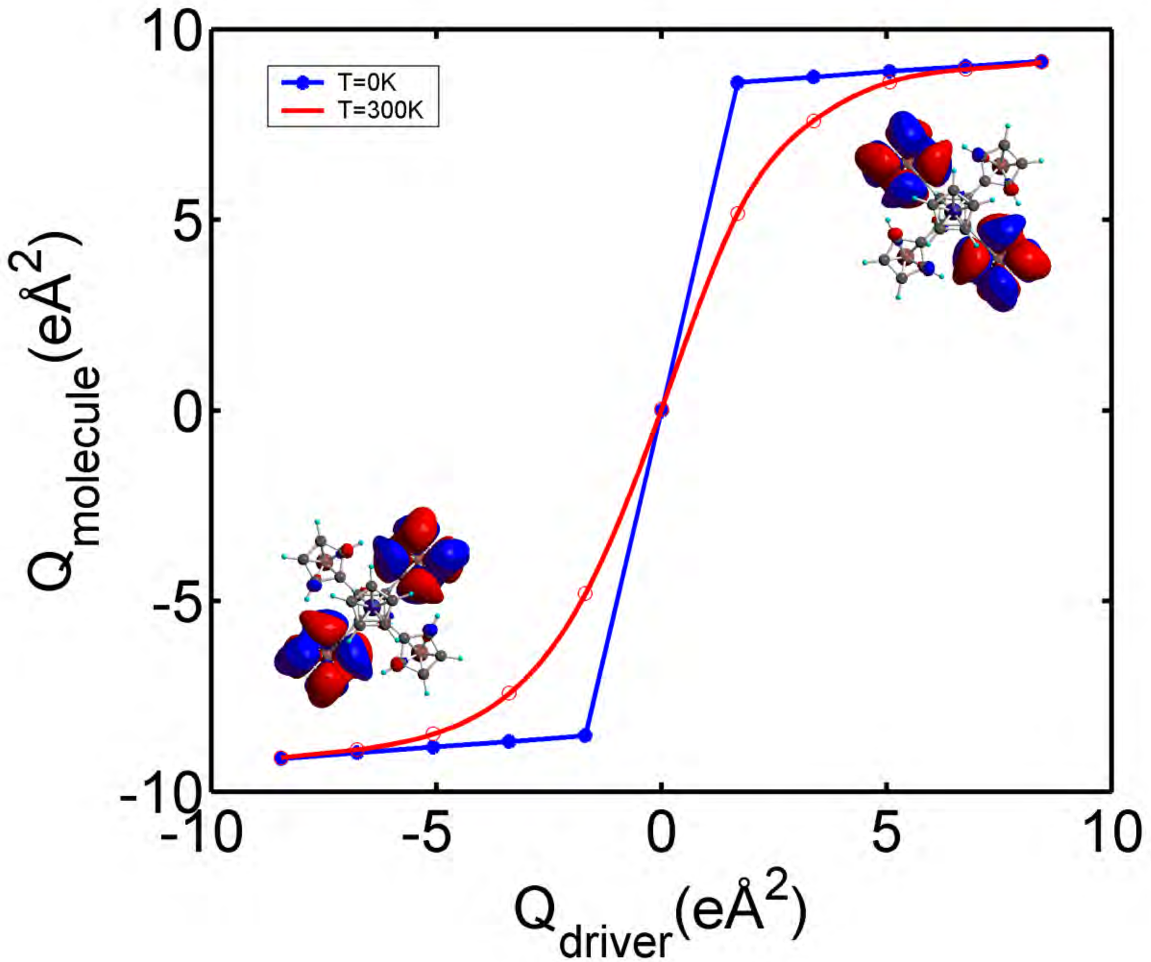
"0"



"1"

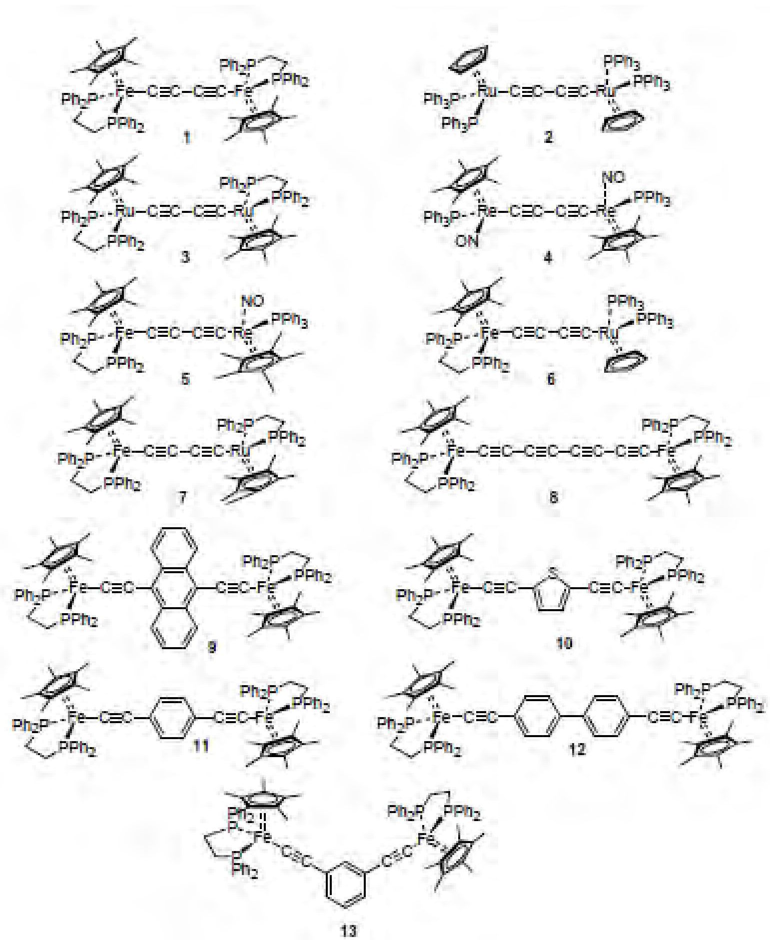
Guassian-98 UHF/STO-3G/LANL2DZ

Switching molecule by a neighboring molecule



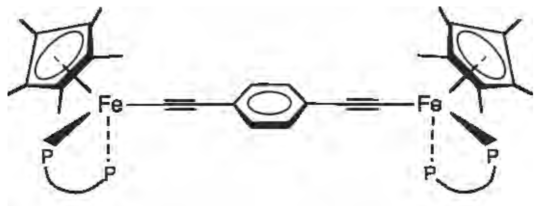
Coulomb interaction is sufficient to couple molecular states.

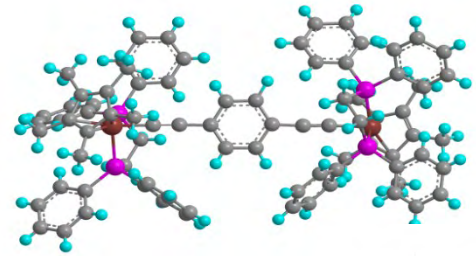
Lapinte group synthesis



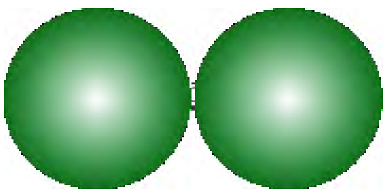
para-Fe2

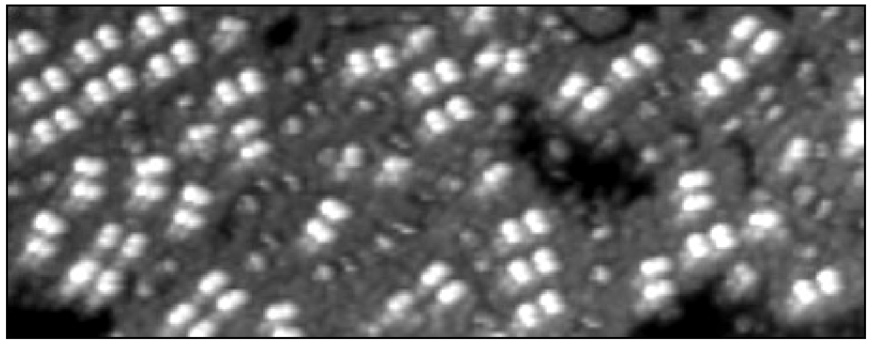
Kandel Group



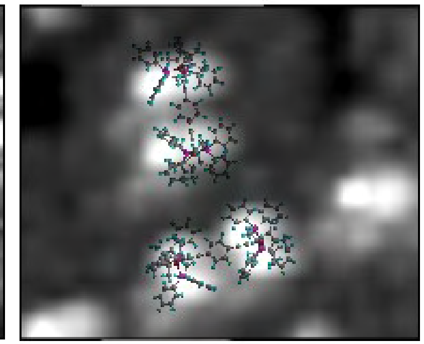


Neutral



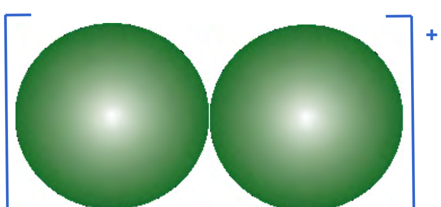


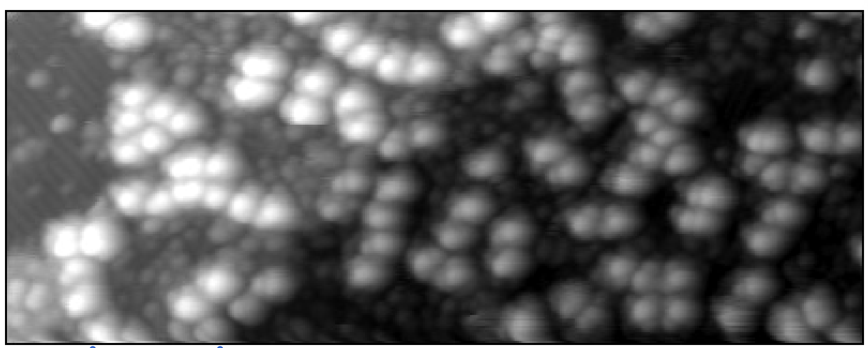
335 Å x 137 Å
-1 V, 5 pA



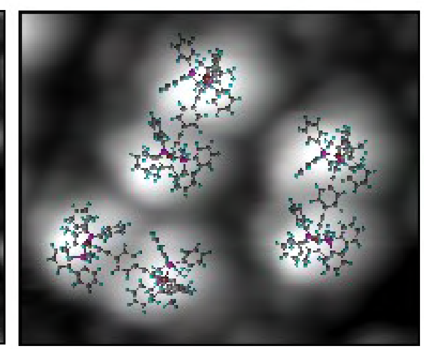
54 Å x 48 Å

Mixed Valence





335 Å x 137 Å
2 V, 10 pA



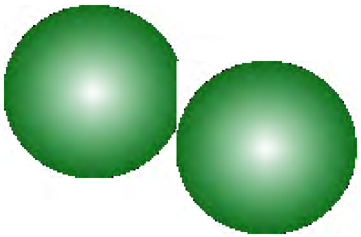
54 Å x 48 Å

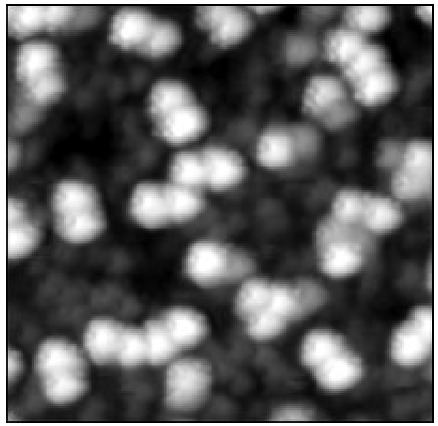
Synthesis: Lapinte

meta-Fe2

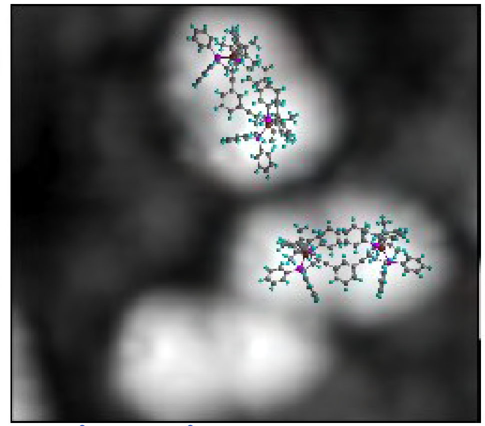
Kandel Group

Neutral

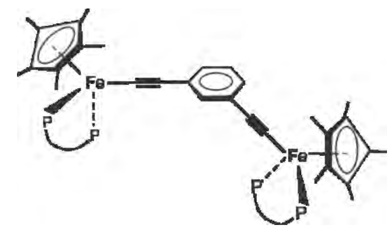




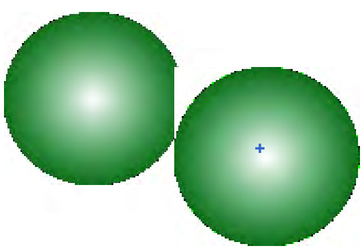
175 Å x 179 Å
0.5 V, 20 pA

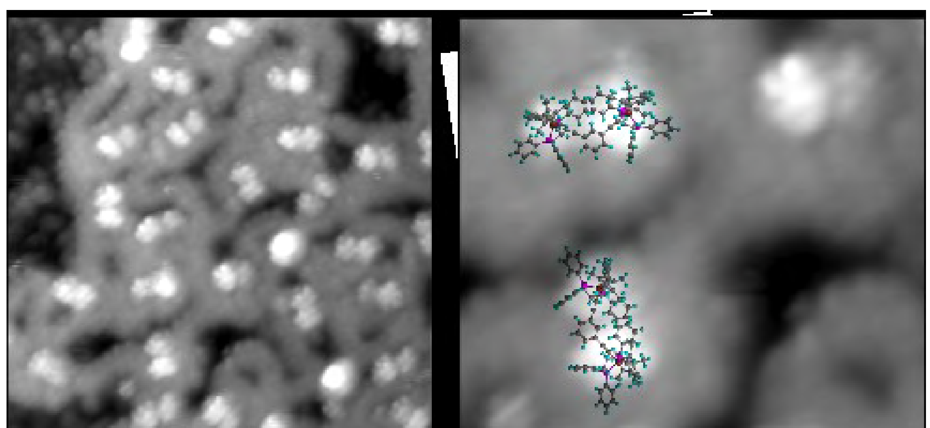


66 Å x 61 Å



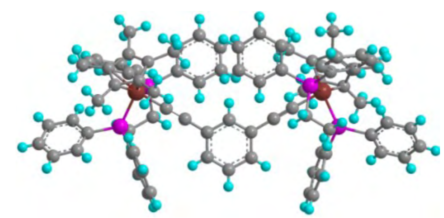
Mixed Valence





175 Å x 179 Å
1 V, 5 pA

66 Å x 61 Å

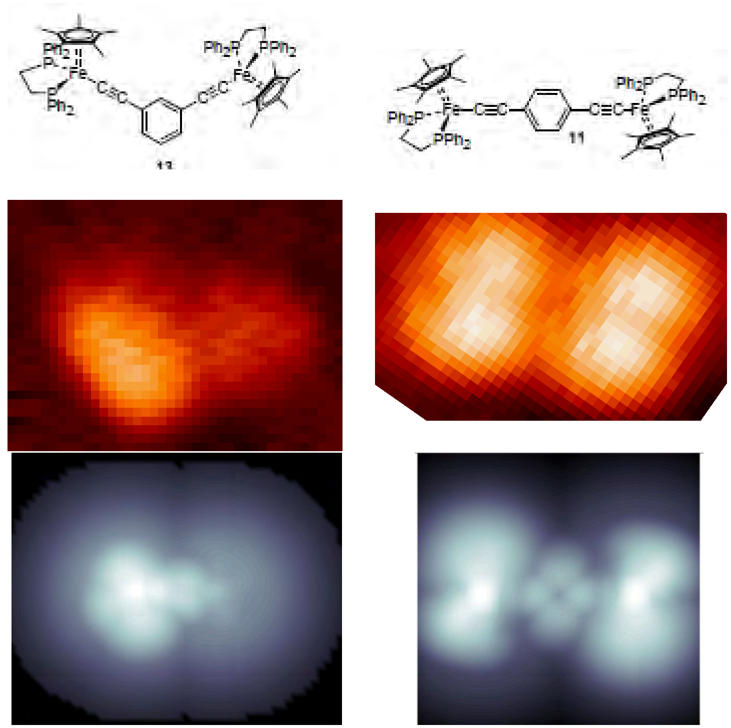


Synthesis: Lapinte

Imaging and modeling STM

image

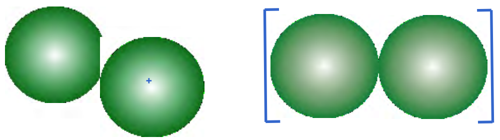
calculation

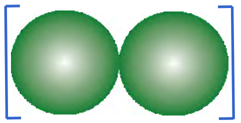


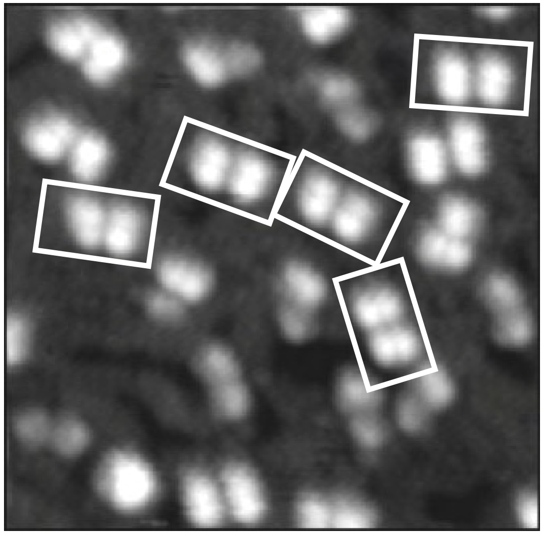
m-Fe2 p-Fe2

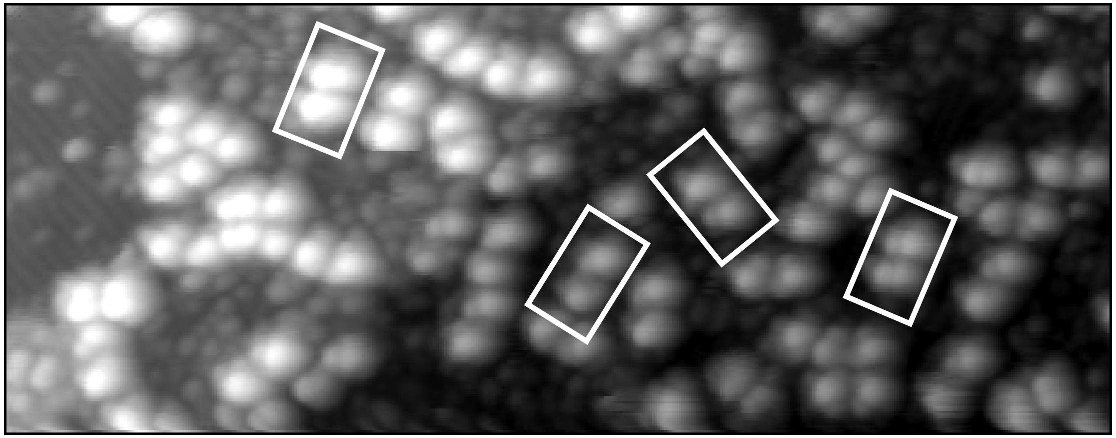
Kandel Group

Mixture of Mixed-Valence *meta*-Fe2 and *para*-Fe2









162 Å x 159 Å
-2 V, 100 pA

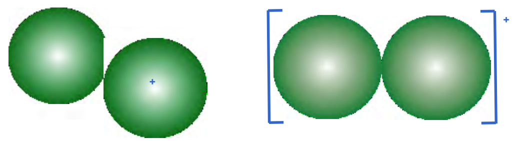
335 Å x 137 Å
2 V, 10 pA

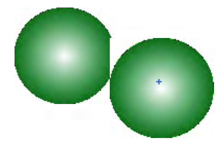
Synthesis: Lapinte

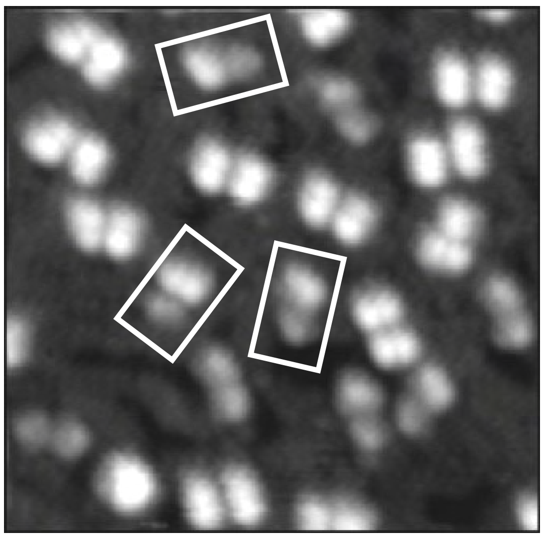
Mixed-Valence p-Fe2 and m-Fe2

Mixed-Valence p-Fe2

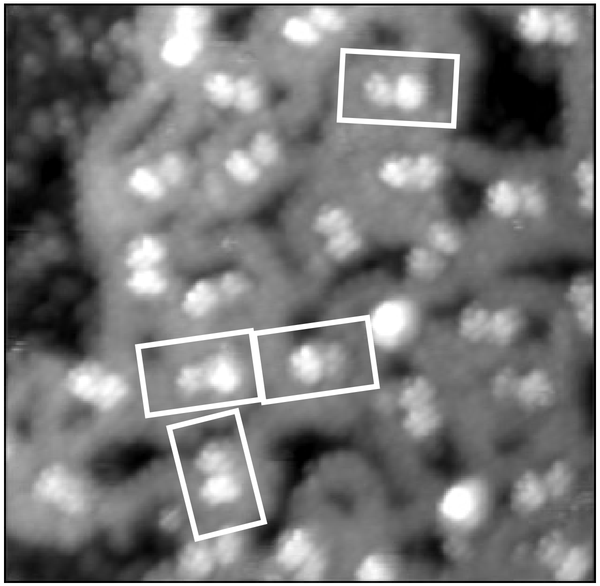
Mixture of Mixed-Valence *meta*-Fe2 and *para*-Fe2







162 Å x 159 Å
-2 V, 100 pA



175 Å x 179 Å
1 V, 5 pA

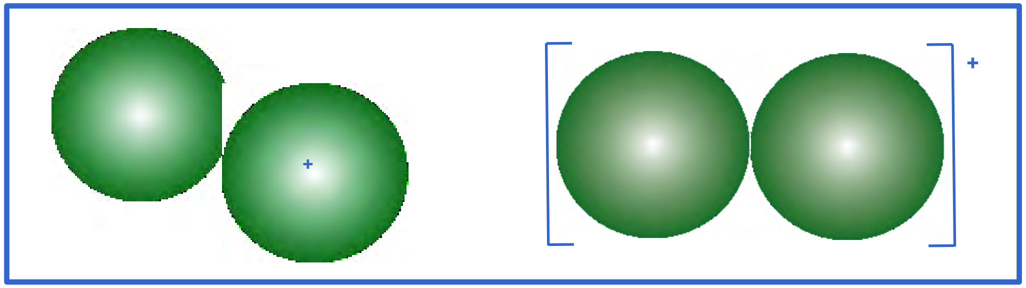
Synthesis: Lapinte

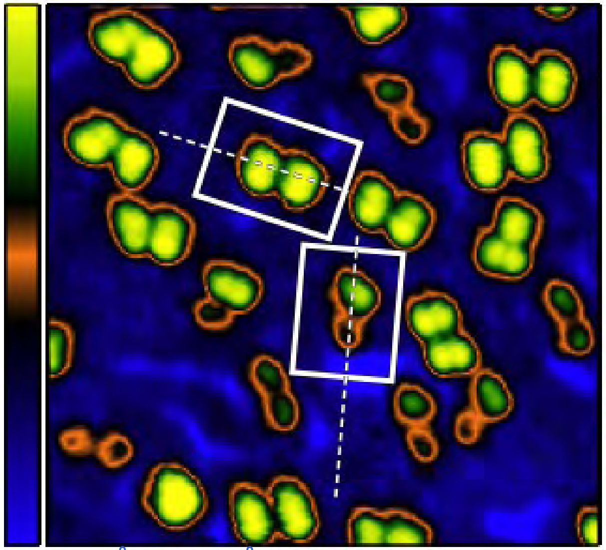
Mixed-Valence p-Fe2 and m-Fe2

Mixed-Valence m-Fe2

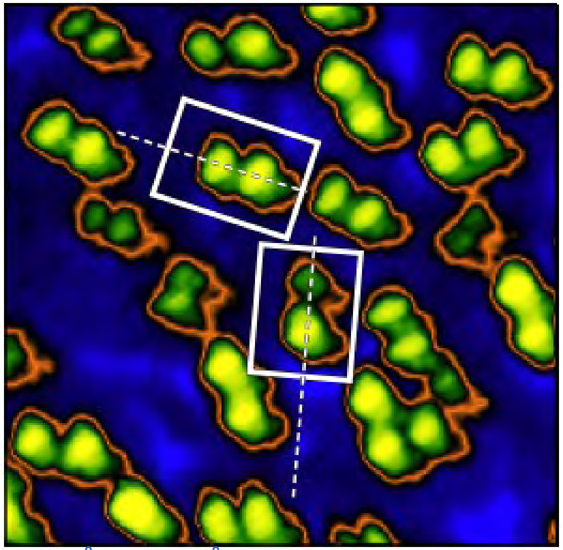
Mixture of Mixed-Valence *meta*-Fe2 and *para*-Fe2

Kandel Group

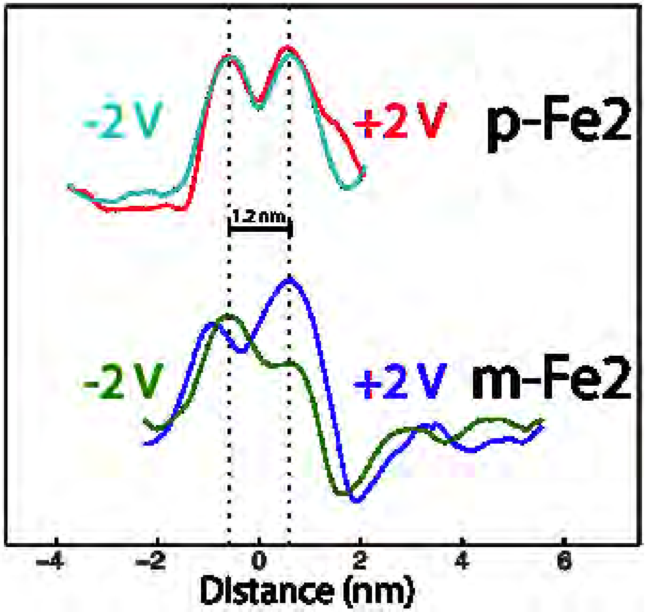




162 Å x 159 Å
-2 V, 100 pA



162 Å x 159 Å
+2 V, 10 pA

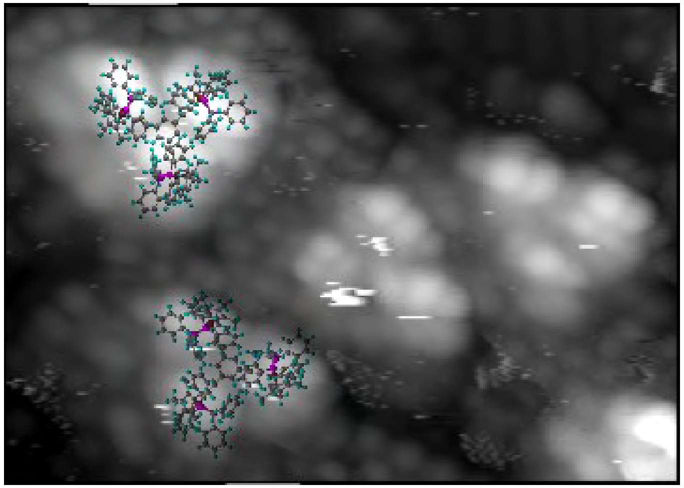


Occupied orbitals

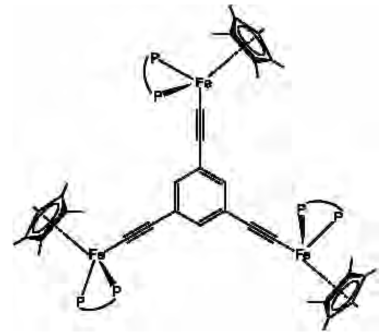
Unoccupied orbitals

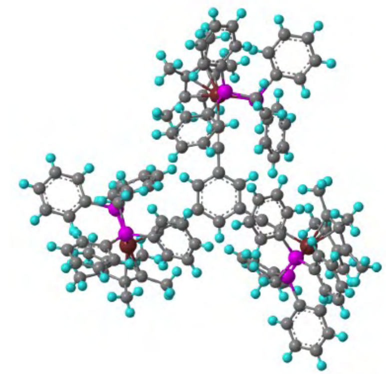
Synthesis: Lapinte

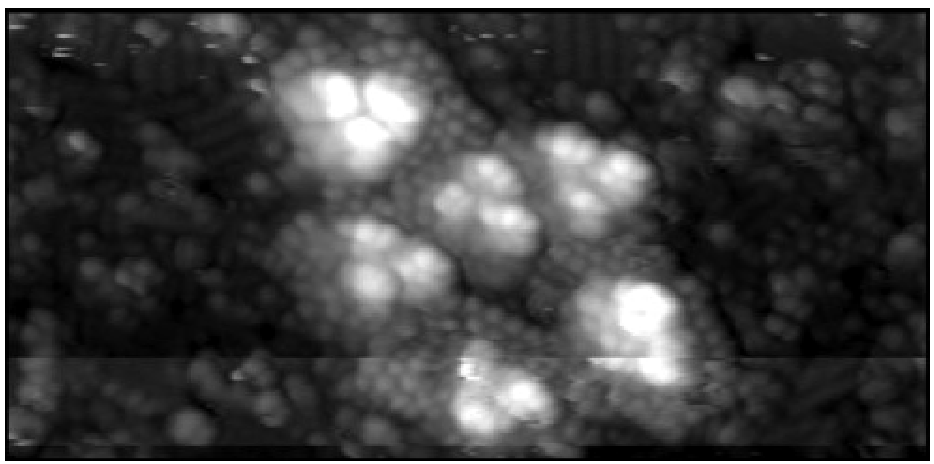
Neutral Fe3



Neutral Fe3, 81 Å x 58 Å
2 V, 10 pA





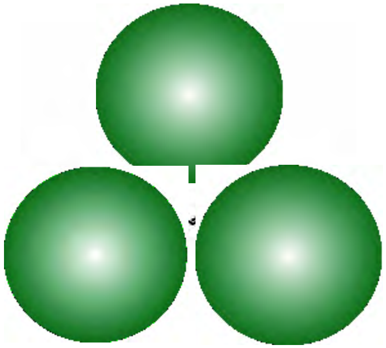


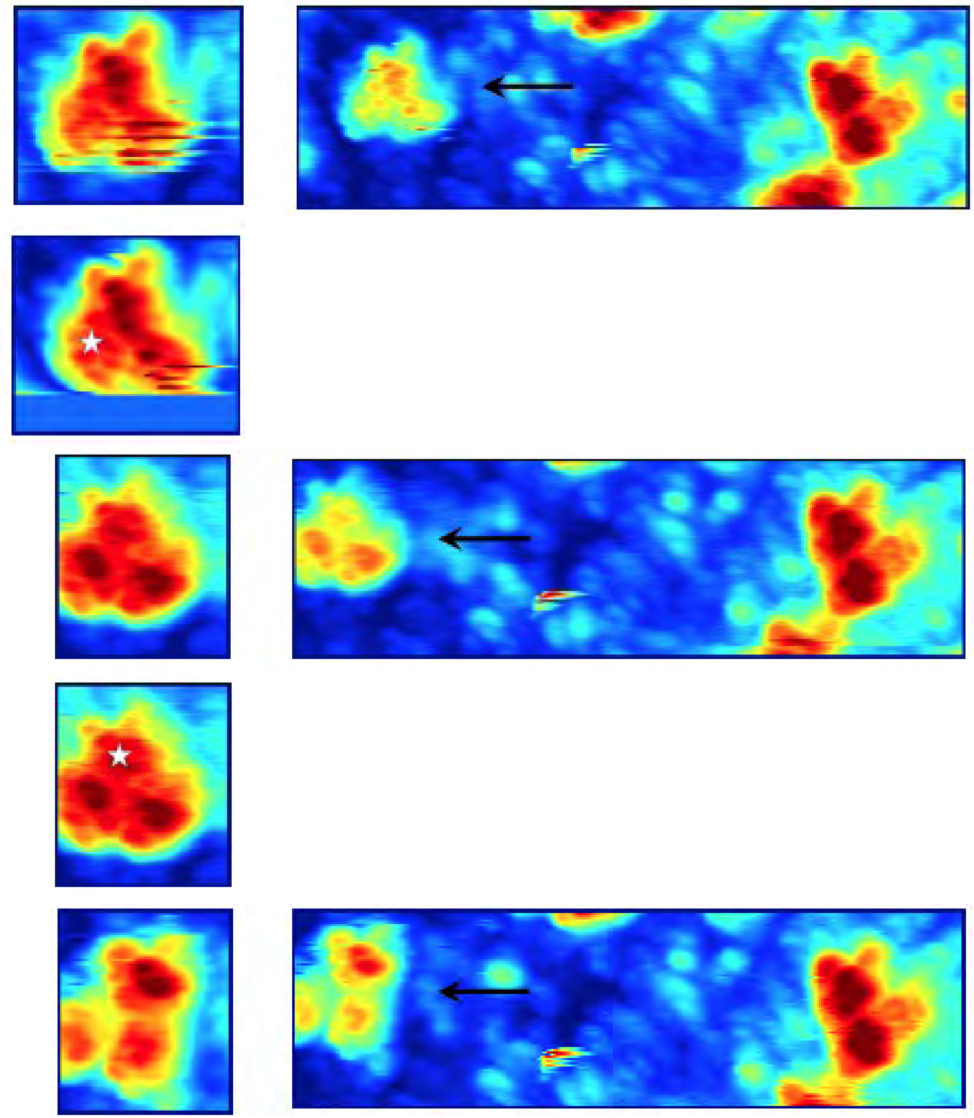
Neutral Fe3, 187 Å x 91 Å
2 V, 10 pA

Synthesis: Lapinte

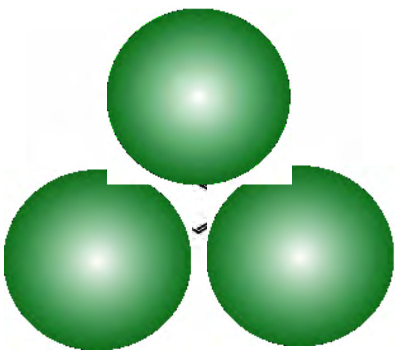
Mixed-Valence $Fe3^{+}$

Preliminary experiments for tip-induced intramolecular electron transfer

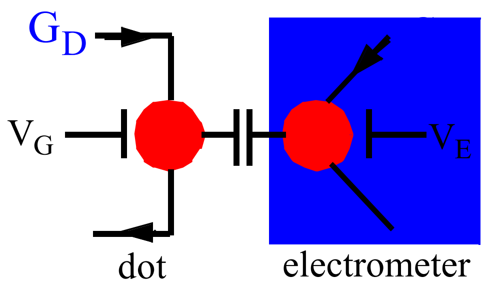




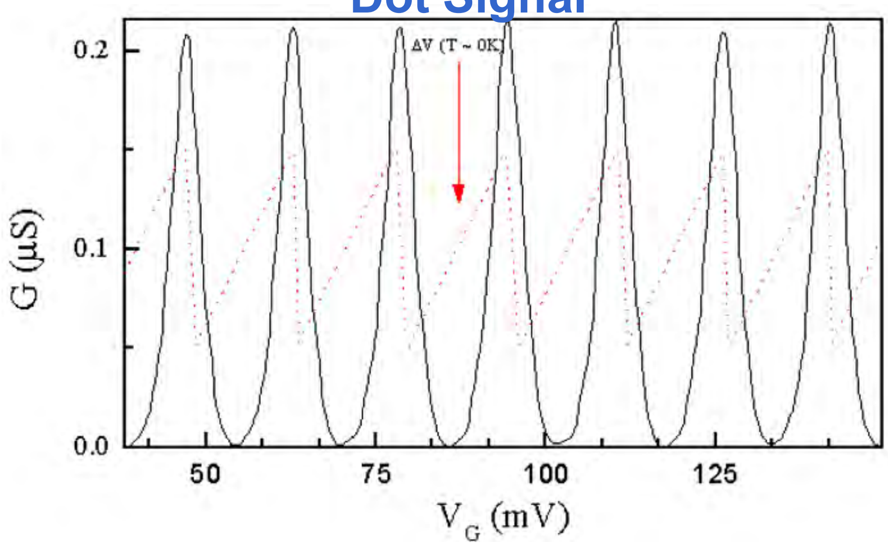
Decrease tip-sample distance (increase tunneling current)

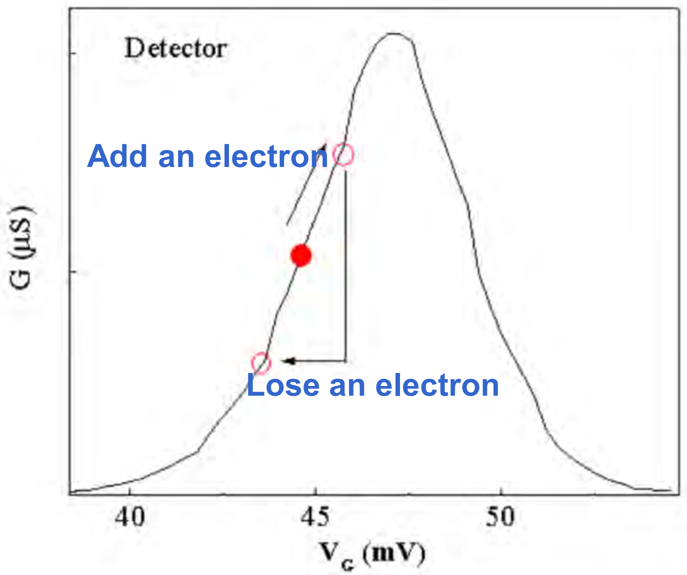


Ultra-Sensitive Electrometers



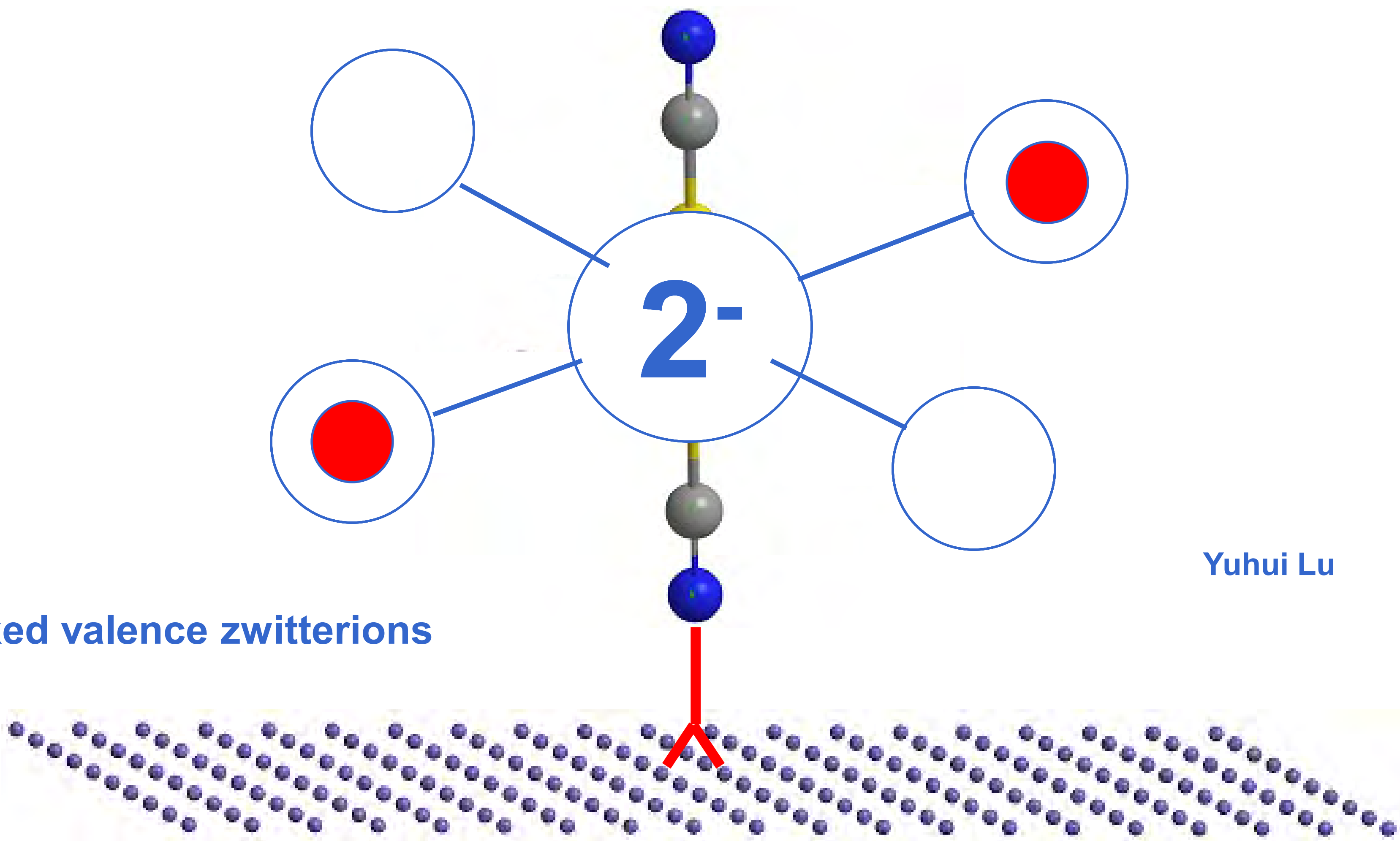
Dot Signal





Dot electrometers can detect 2% of elementary charge.

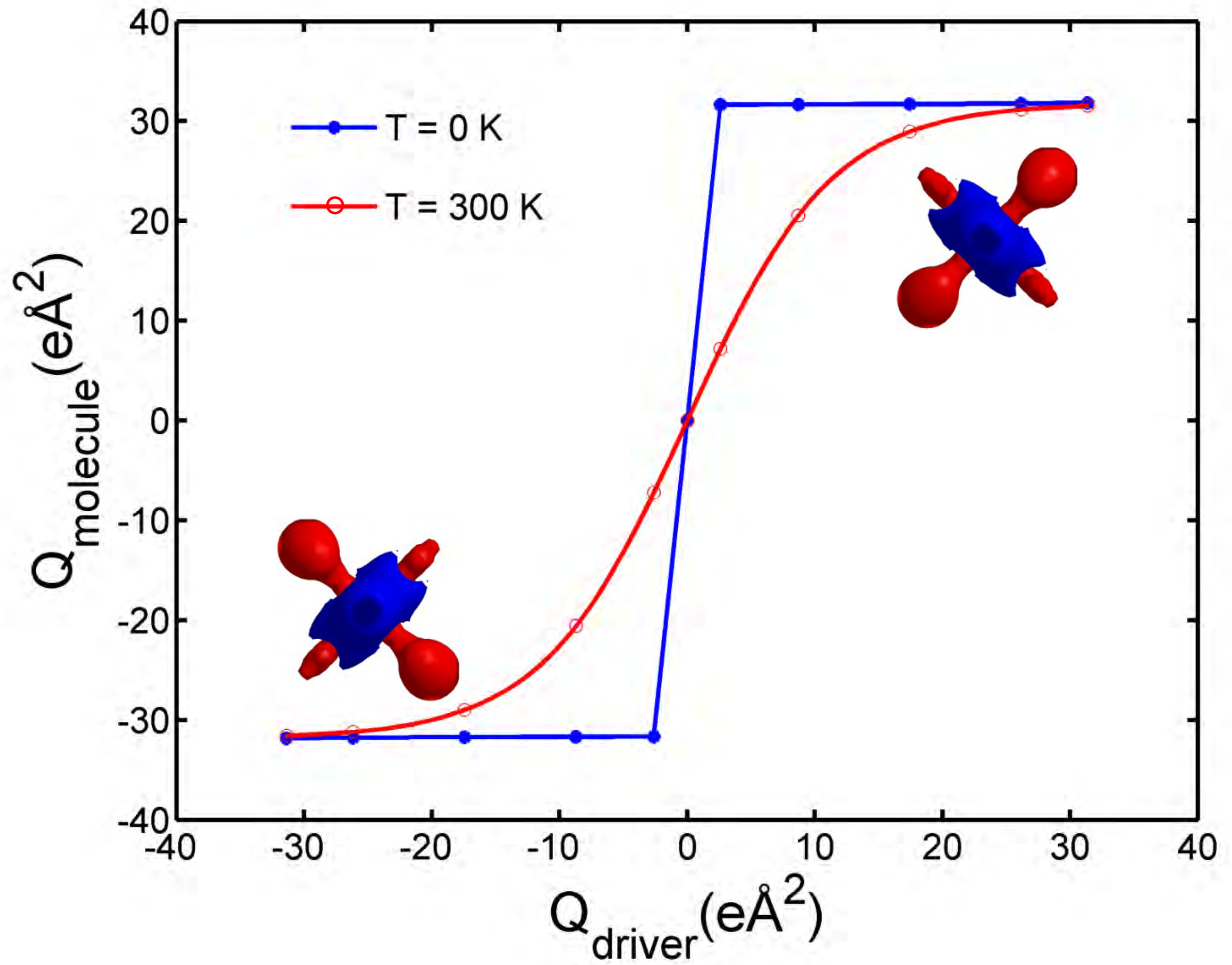
Using *closo*-borate as self dopant



Yuhui Lu

Mixed valence zwitterions

Response function



Mixed valence zwitterions

Coulomb interaction is sufficient to couple molecular states at room temperature.

Requirements for integrated molecular devices

- Ultra-low power dissipation
- Nano-integration: connect many devices together
- Power gain: must restore signal levels stage-to-stage
- Robustness: overcome variations and defects

Conclusions

- QCA offers possible path to limits of downscaling – molecular computing.
  - General-purpose computing
  - Low power dissipation which is essential
- QCA devices: metallic, molecular, magnetic, semiconductor.
- Molecular implementations focus: mixed-valence systems
  - synthesis
  - STM imaging
  - electrical measurement
  - mixed valence zwitterions

Thanks for your attention.