

Molecular Cellular Networks:

A Non von Neumann Architecture for Molecular Electronics

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Abstract—The two fundamental limitations of the present computing paradigm are power dissipation from transistor switching and the architectural von Neumann bottleneck that segregates processing from memory. We examine a cellular architecture which radically intermixes memory and processing, and which is based on a transistor-less approach to representing binary information using the arrangement of charge within the molecule. Representing bits by molecular configuration, rather than a current switch, yields the limits of functional density and low power dissipation. Matching a new computational element to a new architectural framework could enable general purpose computing to evolve along a new roadmap.

Keywords—mixed valence chemistry; molecular electronics; novel materials; non von Neumann architectures; computer architecture

I. INTRODUCTION

We describe a new non-von Neumann cellular architecture that encodes, transmits, and processes digital information represented by the electronic charge configuration of interacting molecules. These molecular cellular networks (MCN) combine molecular quantum-dot cellular automata (QCA), a transistor-less paradigm for single-molecule devices [1], with a new architectural framework that intermixes computation, memory, and transport—breaking the von Neumann bottleneck. The information flow can be dynamically

directed along paths defined by larger-scale clocking electrodes. In a two-dimensional active device layer, bit packets are formed by groups of molecules holding the same binary information. This approach could lead to systems that operate near the fundamental limits of low power dissipation and can enable

general-purpose digital computation with molecular-scale functional densities [2].

We have recently designed and synthesized a new class of molecules with key properties necessary to implement MCN systems [3]. The molecule is a neutral mixed-valence zwitterion with ferrocene centers forming the active (“0” or “1”) dots and a carborane cage forming the null dot. These molecules are “self-doping”—the carborane cage acts as an acceptor, so the mobile charge is generated within the molecule itself. Electrostatic clocking could implement the MCN design to achieve general-purpose computing on a new logical basis.

II. QUANTUM-DOT CELLULAR AUTOMATA

Molecular QCA [4-14] represents digital information at the single-molecule level as shown schematically in Fig. 1. Each dot represents a molecular charge center which localizes a single mobile charge in one of three positions. If the charge is in the central position, the molecule is in the “null” state, while occupancy of the other two positions encodes a binary “1” or “0” respectively. (The orientation difference between the two states is determined by the direction of information flow in the circuit—see Fig. 2.) Switching states involves quantum tunneling between intramolecular sites. Coupling between molecules is through the Coulomb interaction only and requires no transport of particles to move information—neither a charge current nor a spin current needs to flow. Rather, strong intermolecular forces couple the electronic charge configurations of neighboring molecules.

The information flow can be dynamically directed along paths defined by larger-scale clocking electrodes as shown in Fig. 2(a). The logically repeating unit is the molecular pair shown in Fig. 2(b) as colored squares holding either bit. The motion of the bit packet is governed by the perpendicular electric field which sweeps across the molecular layer. This is not diffusive or ballistic motion, but rather clock-controlled. The switched cells are always near their instantaneous ground state (quasi-adiabatic switching) with the consequence that power dissipation can approach the thermodynamic limits.

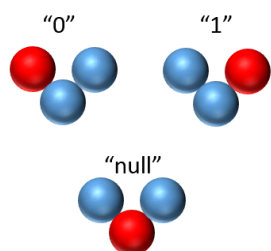


Fig. 1. Representing digital information by the charge configuration of a molecule.

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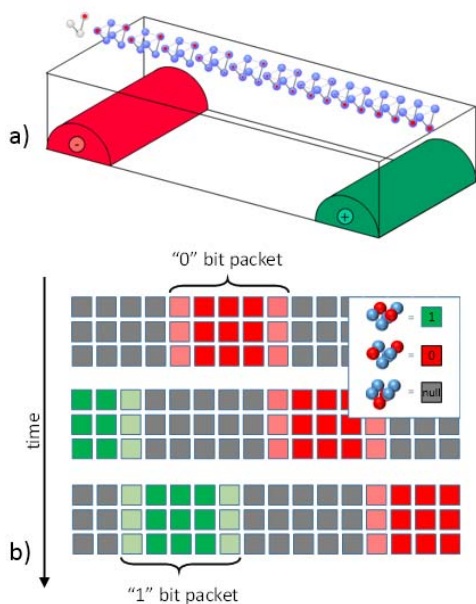


Fig. 2. Clocking of molecular devices. (a) Schematic of buried clocking electrodes switching the activity of surface-deposited molecules. A shift register is shown (one molecule wide for clarity). (b) Snapshots of a strip of digital molecules which encodes information in molecular charge configurations. Bits are moving left to right.

Non-molecular single-electron implementations of QCA have been created which act as prototypes for the molecular realization. Functioning metal-dot QCA cells have been fabricated as well as several devices and more complex circuits [15-26]. In these experiments aluminum islands act as the dots, and they are coupled by aluminum oxide tunnel junctions. The evaporation technique used produces capacitances that are still relatively large, so these experiments needed to be performed at millikelvin temperatures. Key experimental milestones in metal-dot QCA include: transmission of a signal down a QCA wire; operation of the first QCA logic element, a three-input majority gate; fabrication of a clocked QCA cell (Figure 3); operation of a clocked cell as a single-bit memory; measurement of power gain in QCA; and demonstration of fan-out in a clocked QCA shift register. The major drawback of these prototypes is the limitation of cryogenic operation, whereas molecular implementations would operate at room temperature. In the molecular version, evaporated metal islands are replaced by individual metal atoms in a molecule.

QCA has also been implemented in semiconductors. QCA functionality has been demonstrated in GaAs dots formed by a depletion top-gate structure [27] and in silicon nanostructures [28]. The Wolkow group has shown room temperature QCA operation in silicon dots formed by single dangling bonds at molecular-scale sizes [29]. Because of their small size, these cells function at room temperature.

III. DESIGNING MOLECULES

The role of the “dot” in molecular QCA is played by a redox center in a molecule. QCA molecules have more than one redox center arranged in the proper geometry—

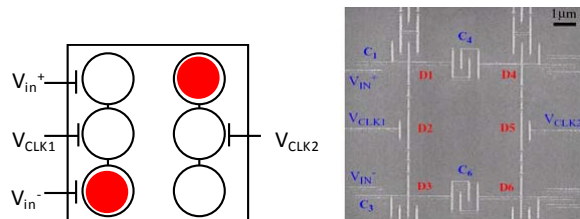


Fig. 3. Clocked metal-dot QCA cells.

either double-dots, triple dots (for clocking) or squares. If each redox center is chemically equivalent, then the configuration of charge among the centers is determined by the external local electric field. In a functioning QCA molecule, this “driver field” would be due to either the charge configuration of a neighboring molecule or that on a nearby conductor providing input at the edge of the array. An important focus here is on the way specific molecules respond to the symmetry-breaking driver field.

Mixed valence complexes are compounds which contain more than one redox center and exhibit electron transfer between different redox centers. Starting with the pioneering work of Creutz and Taube [30], the study of these multiple redox center compounds opened the new field of the chemistry and physics of mixed valence complexes. A large variety of mixed valence complexes have been synthesized and their properties are well studied. Comprehensive reviews have been written by Creutz [31], Crutchley [32], Meyer *et al* [33] and Ceccon *et al* [34].

A. Charge localization

An important aspect of mixed-valence molecules is the extent to which charge is localized on one redox center or another. If we take a two-dot molecule as paradigmatic, we can describe the mobile charge as being on the right or left dot, with switching accomplished by tunneling through the barrier formed by the linking group. A reduced 2×2 Hamiltonian can then describe the system, with off-diagonal elements H_{ab} specifying the effective hopping matrix elements between the two sites. If the nuclear positions in the molecule were completely fixed, the system would be isomorphic to the familiar double well potential. In the absence of an applied field, the symmetric ground state and antisymmetric first excited state split in energy by $2H_{ab}$. A neighboring polarized molecule will shift the on-site energies of the two dots by an energy Δ determined by electrostatics and geometry. If this driving energy Δ is considerably more than this splitting, the charge will be effectively localized on one side or the other by the applied field. Thus the first criterion for QCA molecular operation is simply that the coupling energy H_{ab} is sufficiently small compared to Δ to support this localization. The tunneling energy also sets the time scale for charge transfer in the molecule. The charge transfer time in molecules can be tuned by selecting different linking groups. Fortunately, there is a very large design space: across mixed-valence chemistry the electron transfer time varies by 20 orders of magnitude [35]. It is relatively easy to achieve good localization and still have switching speed in the THz range.

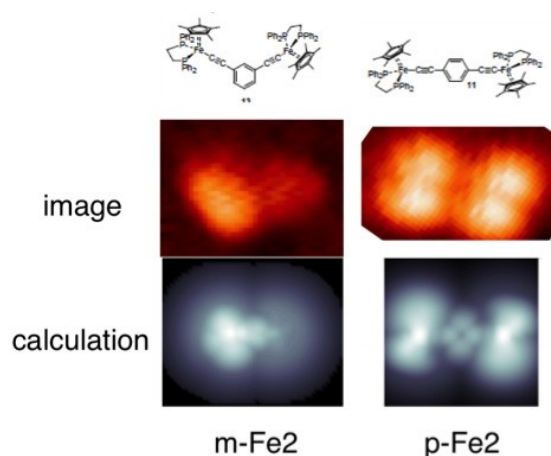


Fig. 4. UHV STM image of meta and para forms of symmetric mixed-valence molecules.

We have seen that changing the linking group can have a significant effect on the localization of charge in the molecule. Double dot molecules Ru_2 ($\text{trans}[\text{Cl}(\text{dppe})_2\text{Ru}(\text{CC})_6\text{Ru}(\text{dppe})_2\text{Cl}]$), and Fe_2 ($1,3\text{-}\{\text{Cp}^*(\text{dppe})\text{Fe}(\text{C}=\text{C})\}_2(\text{C}_6\text{H}_4)$), were synthesized in multiple forms. [36, 37] Fig. 4 shows two molecules, para- Fe_2 and meta- Fe_2 , imaged under identical conditions. These two molecules have *identical* metal-ligand dot structures, and the linkers are equivalent except for their geometry about the central benzene ring. The difference in geometry creates a dramatic difference in the electronic coupling across the molecule, with a significantly lower barrier to electron transfer for p- Fe_2 . Images of these molecules, with both compared side-by-side in their mixed valence states, demonstrate the consequences of this geometrical change. Mixed valence m- Fe_2 is strongly charge-localized, consistent with a sizable barrier to intramolecular electron transfer, while mixed valence p- Fe_2 appears symmetric (*i.e.*, charge delocalized) under identical imaging conditions. Reversing the bias voltage between the tip and the sample proves that the difference between the two molecules is indeed electronic in nature—the observed contrast reverses.

We have seen evidence for inter-molecular charge interaction as well. Fig. 5 shows that the asymmetry of the mixed-valence Ru_2^+ charge distribution creates long-range order in the monolayer island. We observe that within rows of molecules, the charge asymmetry is anti-correlated; that is, each molecule flips into the opposite charge state as its neighbor—exactly the expected and desired behavior for digital QCA molecules.

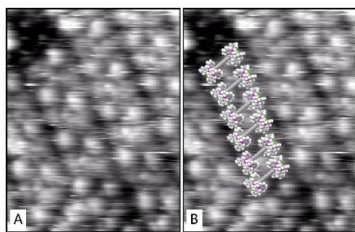


Fig. 5. Island of close-packed Ru_2^+ . Intermolecular forces order the mixed valence molecules according to charge, producing a zigzag array of bright and dim dots.

Furthermore, there is long-range order in the monolayer island that spans multiple molecular rows, and we conclude that adjacent rows

must influence each other's charge distribution.

All discussion of charge localization must, of course, bear in mind the time scale of the localization. Figure 4 shows no localization in the STM images of the para compound, but the time scale for imaging is minutes and the driving potential that breaks molecular symmetry is in this case accidental (whatever was on the surface nearby). It may be that a stronger driver, from a similarly polarized molecule, and a higher speed measurement would show localization in this case as well. The combination of instrumental perturbations and DC measurement might simply mask the intrinsic bistability.

B. Nuclear relaxation

Molecules are not rigid structures and the transfer of an electron from one dot to another inevitably causes a slight but energetically significant shift in the nuclear positions of the whole molecule. Furthermore, if the molecule is in solution the solvent molecules that surround the target molecule will also respond to the shift in the electronic charge distribution occasioned by the electron transfer. The simple 2×2 Hamiltonian that describes the electronic system must therefore be coupled to the nuclear degrees of freedom. It is usually sufficient to parametrize this nuclear degree of freedom with a single electron transfer (ET) coordinate which is, say, 0 for the ground state with charge is on one dot and 1 when the charge is on the other. The relaxation of the nuclear degrees of freedom lowers the energy and could potentially trap the charge on one site in a parabolic well. The excitation of this parabolic energy surface is the harmonic vibrational mode of the molecule around the charge-localized energy minimum. The nuclear relaxation around the localized charge is characterized by the reorganization energy λ which is defined as the energy cost of the electron being on the “wrong” side of the relaxed double-dot structure, as shown in Figure 6. With no applied bias a potential barrier of $\lambda/4$ forms between the trapped state and the

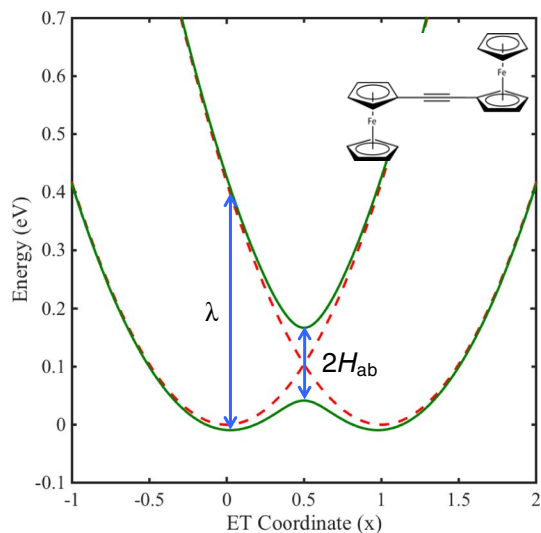


Fig. 6. Adiabatic (green) and diabatic (red) potential energy curves for electron transfer in the diferrocenylacetylene (DFA) mixed-valence molecule computed with constrained DFT. λ and H_{ab} are the reorganization energy and electronic coupling, respectively.

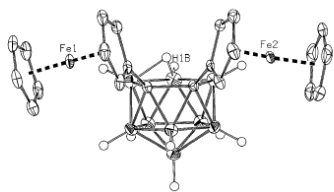


Figure 7. ORTEP plot of the neutral mixed valence zwitterion $Fc^+FcC_2B_9^-$.

switched state. Clearly then, another requirement for QCA switching is that the driving energy Δ be larger than $\lambda/4$ so the represented bit is not stuck [38, 39].

In the chemistry literature focus is typically on behavior in solution where the bistability frequently involves the solvent environment (so called “outer sphere” relaxation) as well as the intrinsic molecular relaxation (“inner sphere”). Our interest lies in molecules adsorbed or bonded to a surface without a solvent but with the complications, and potential rigidity, of an underlying substrate. In that case the support of the substrate will change the nuclear relaxation and may make it play even less of a role.

C. Self-doping molecules

The mobile charge in mixed valence molecules is almost always the result of oxidation or reduction of a neutral precursor molecule, requiring the creation of a counterion in the vicinity to provide a neutralizing charge. The presence of the counterion may produce an uncontrolled bias to the molecular charge configuration. Sometimes the counterion can apparently be washed off and the neutralizing charge provided by the bulk surface charge [9]. Even in that case, it would be preferable to have a neutral mixed valence molecule so that no extraneous charge is attracted.

We have recently designed and synthesized a class of new molecules that are in a mixed valence state though they maintain overall charge neutrality [40]. The carborane 7-Fc⁺-8-Fc⁻-7,8-nido-[C₂B₉H₁₀], $Fc^+FcC_2B_9^-$, was targeted since it combines several attractive features as a molecular switch for QCA applications. Specifically, the carborane unit carries a charge which balances that of the ferrocenium, the carborane bridge allows for electron transfer between the Fe^{II} and Fe^{III} centers, and finally, an all-neutral null state is possible. The null state, where the charge is symmetrically distributed as two ferrocenes and a neutral carborane, is an important element for

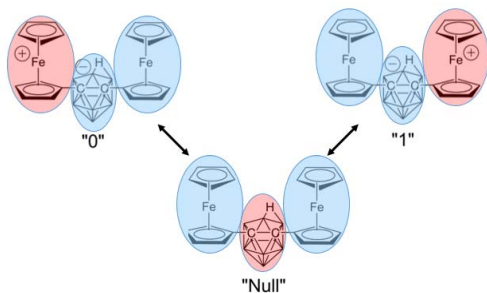


Fig. 8. The switchable mixed valence zwitterion $Fc^+FcC_2B_9^-$.

digital materials. Since the counterion is located at the geometrical center of the molecule, the counterion effect is equivalent with respect to both end sites where the mobile charge can localize. The crystal structure of this first generation neutral mixed-valence molecular framework is shown in Fig. 7.

These molecules moreover have the central null dot necessary for clocking and employment in the MCN paradigm. Here the null dot is formed by a carborane cage, and the active (1 and 0) dots are formed by ferrocene groups. This molecule is a *neutral* mixed valence zwitterion, avoiding the complications of an external counterion. The counterion is in fact built into the molecule itself via covalent bonds and in a position that does not bias the 1 or 0 configuration. The molecule is “self-doping”—the carborane cage acts as a built-in acceptor [40-42] with the mobile hole residing on one ferrocene group or the other to represent the bit.

The structure and the mechanism of charge transfer of the system has been unambiguously characterized by a combination of ensemble measurements (cyclic voltammetry, UV-Vis near IR spectroscopy, single crystal X-ray analysis, EPR, multinuclear NMR spectroscopy) and constrained-DFT calculations. In all respects, this molecular framework appears to be an excellent candidate to build upon for digital molecular materials. One particularly attractive feature is the ready ability to chemically modify and tune the system to enable the incorporation of supramolecular directing units and/or surface attachment groups.

IV. BEYOND VON NEUMANN ARCHITECTURE

The first step in developing architectures for this beyond-transistor paradigm has been to design functional units which stepped beyond the transistor-based representation of information, while retaining the overall system architecture that is familiar. Considerable effort has gone into this, aided by the availability of circuit-level design tools like QCADesigner [43]. Kogge and Niemi designed the first simple microprocessor in QCA [44] shown in Fig. 9. A significant literature by multiple groups has begun to explore how to implement basic computational elements: adders, multipliers, ALU's, etc. [45-50]. These valuable contributions have focused on circuit-level design rather than the overall computational architecture issues.

The traditional von Neumann computational model assumes separate subsystems of memory and logic, with a well-defined interface between the two. Further, the key state defining a computation – a thread – resides firmly in the logic and executes individual computations in some sequential, well-defined parallel order. When parallel

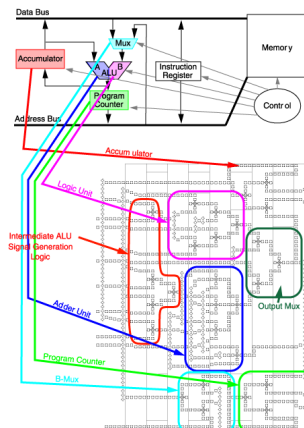


Fig. 9. The Simple-12 microprocessor design using QCA.

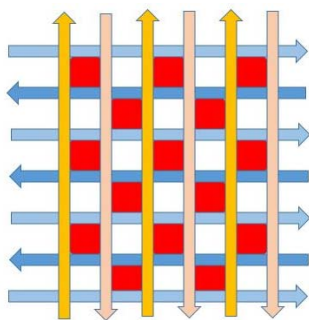


Fig. 10. A cellular computational network connects an array of computational resources with directional information transport paths. It is designed as a universal molecular QCA clocking floorplan, creating the molecular cellular network (MCN) architectural framework.

systems are constructed, there are multiple combinations of logic and memory, and a thread, once started, almost never leaves the site of its birth. Modern semiconductor technology has evolved to efficiently support this model.

The molecular QCA technology discussed here has a much different set of computational attributes. Individual devices have both inherent logic and memory functionality. There is no equivalent of a “wire” that holds only one value at a time. Data transferring from one place to another moves inherently through a pipeline of clocked devices, upping the throughput of the wire to be a function of the clock rate of the devices, not its length. Blindly using such technology in conventional von Neumann architectures is of course possible, but doesn’t efficiently use the technology’s capabilities.

Breaking the von Neumann bottleneck requires a more revolutionary architectural approach, exploiting the local memory and interconnectivity potential of QCA devices. The architectural framework, shown schematically in Fig. 10, accomplishes this by connecting computational cells (nodes) with active transport paths. Each processing cell, shown in red in the figure, can contain both memory and digital logic. The computational cells are at a much larger scale than the QCA single-molecule cells. The transport paths are active QCA shift registers which can also process information as it moves from node to node.

Fig. 11 shows the clocking scheme for a molecular implementation of this cellular network framework using QCA. The figure shows the calculated perpendicular clocking field from a regular array of clocking wires which forms a rich 2D arrangement into which key architectural features can be incorporated. Brighter areas show active regions (see Fig. 2) where molecular QCA cells hold information. The pattern moves as the clocking field transports molecularly encode data and processes information en route. Alternating rows of QCA logic cells move information in opposite directions. This permits feedback of intermediate values back into earlier logic stages. In addition, with proper timing, these alternating rows also create alternating columns, where data can proceed either “up” or “down” the array. Such directionality supports longer range timing delays needed for global data synchronization.

Several promising programmable non-von Neumann approaches can be supported by this architectural framework.

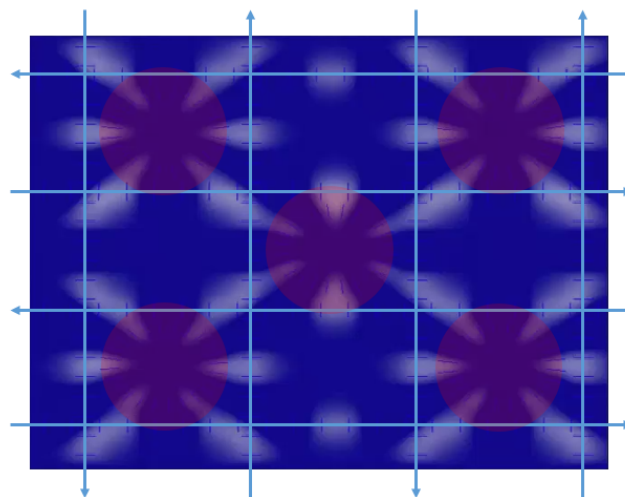


Fig. 11. A non von Neumann computational architectural framework, implemented for clocked QCA. Small dark blue line segments represent the buried clocking electrodes (see Fig. 2). The light shading is the calculated electric field which clocks the molecular device layer on top. Purple circles indicate the computational core/memory cells, and the multidirectional data transport and processing lines are indicated by superposed light blue lines. Memory and information processing function are thoroughly integrated throughout. Individual molecular cells holding data are at a much smaller length scale.

The well-known *systolic array architecture* is a 2D arrangement of identical computational units where data flows in from the edges and proceeds in well-defined waves through the units [51, 52]. A rich set of applications has proven amenable to such arrangements. In nanotechnologies like QCA such an architecture is a direct match, as the timing constraints of the system are virtually solved once the individual unit is designed. Further, given the potentially very high clock rate possible, we need not design such units as conventional parallel data flows. Much simpler serial function units eliminate much of the timing complexity and allow individual data operands to proceed a bit at a time on the same QCA “wire.” The “*bouncing threads*” model [53-55] keeps the idea of a sequential thread, but eliminates the need for a fixed execution site. A large parallel memory is constructed where each “word” is a loop of QCA wires, with an access point that is essentially a simple serial processor for threads with very small states (variations of a simple accumulator model). Instead of a fixed CPU making memory requests and waiting for a result, a bouncing thread carries the state of the requesting thread to the specific memory loop, where the desired operation is carried out serially, then moves serially out to the memory holding the next instruction, fetching it and then repeating the process. A large memory can thus have a large number of such threads moving through the memory simultaneously. Another strategy adopts the concept of *combinators* from functional models, where expressions are built from a small set of basic operators that “rearrange” the expression text in well-defined fashions [56-57]. Again serial representations of expressions are good matches to QCA. Such architectures are also very compatible with implementations that possibly employ reversibility [58-59] to lower energy costs.

V. DISCUSSION

The fundamental concept behind MCN is to combine the representation of information used in molecular QCA with an architectural framework that is both suited to molecular implementation and avoids the von Neumann bottleneck. For robustness at molecular scale it is important that the technology has true power gain, supporting fan-out and signal restoration [60]. Low power dissipation is also essential because at molecular densities a few nanowatts of heating per device is too much. Quasi-adiabatic clocking of molecular QCA could yield an energy dissipation of less than $k_B T$ per device, while retaining a bit storage energy of many times $k_B T$. [2, 61]

Multiple challenges exist to realizing practical MCN designs. Much remains to be understood about the chemistry of electron transfer in this context. Most of the chemistry literature focuses, understandably, on electron transfer that is either caused by random thermal motion in solution or else by photon absorption. Intramolecular transfer that is driven by the electric field from neighboring molecules arranged on a surface raises new questions.

In addition to having appropriate geometry and charge transfer properties, molecules must be synthesized with anchoring ligands for surface attachment and orientation. Some degree of local self-assembly, probably mediated by hydrogen bonds between molecules, will be necessary to bridge the gap between the molecular scale (~ 1 nm) and the lithographic scale (~ 10 nm).

Input and output to molecular devices is challenging. Coercing an edge molecule into the right state may be as straightforward as using pairs of carbon nanotubes or other nanowire techniques to generate a quadrupole moment in the local field. Clever techniques for using the clock signal to select an appropriate input have also been developed [62]. Detection of single charges is a strength of single electron transistors and careful methods that avoid background charge motion are being developed [63].

The need for an integrated device and architecture for advancing computation to the molecular scale is by now quite clear. We cannot reproduce transistor action with single molecules without disastrous power dissipation consequences. A new approach that retains the power of digital computation and yet enables general-purpose computing will take some effort and further creativity to realize, but may be well worth the exertion.

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