

Reports

A Molecular Shift Register Based on Electron Transfer

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An electronic shift-register memory at the molecular level is described. The memory elements are based on a chain of electron-transfer molecules and the information is shifted by photoinduced electron-transfer reactions. This device integrates designed electronic molecules onto a very large scale integrated (silicon microelectronic) substrate, providing an example of a "molecular electronic device" that could actually be made. The design requirements for such a device and possible synthetic strategies are discussed. Devices along these lines should have lower energy usage and enhanced storage density.

AN APPRECIABLE LITERATURE HAS accumulated about man-made computing devices at the molecular level (1-6). At this level, the "state" of a molecular computing element (10 to 15 Å in size) is changed by altering the structure of a molecule (its conformation, oxidation state, and so forth). This work is motivated, in part, by the facts that "molecular" computation takes place in biological systems, that one understands how to build molecular size "wires," "p-n junctions," and "transistors," and that strategies from molecular biology and the theory of computation explain how to perform essentially error-free computation with error-prone devices. These ideas suggest building a molecular level chip having a device density thousands of times larger than conventional very large scale integrated (VLSI) chips. However, the absence of specific and detailed suggestions for device structure and function has led to justified pessimism about this field (3).

This report describes a molecular-level shift register with a memory density of 100 to 1000 times that obtainable with ordinary VLSI technology. A shift register is a form of memory, consisting of memory cells connected in a line. Each cell stores one bit of information. During each clock cycle, the contents of each cell are shifted to the next register to the right. The first register receives a new bit of information to be stored, while the bit that was in the last register is transferred to the external circuit. The infor-

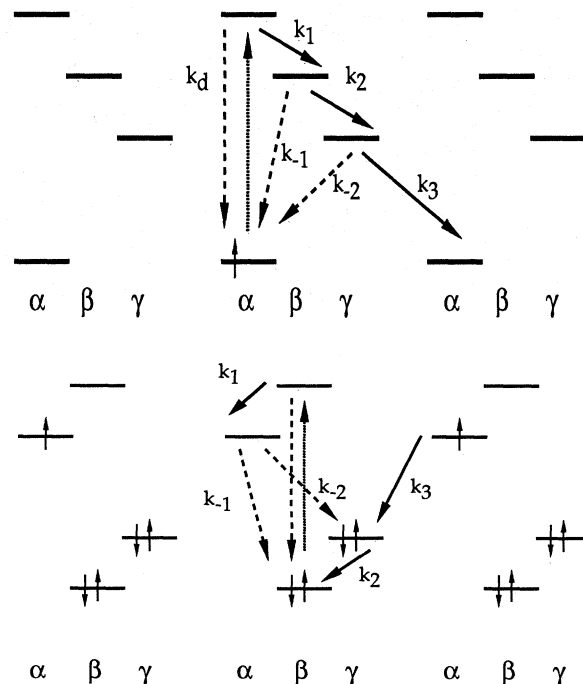
mation storage cells in electronic shift registers generally involve two storage sites to achieve reliable copying of information without confusion. Electronic shift registers are in commercial use as circuit elements for a variety of time-delay and information storage uses. Magnetic bubble memories are a form of shift register.

The molecular shift-register memory is conceived as a physical hybrid between a VLSI-style circuit (7), which is the substrate, and the molecular devices. The major conceptual problems associated with the design of such a chip include: the means of delivering the energy needed for the compu-

tation to the molecules, delivery of the clock signal to the device, fabrication of the molecular device, communicating the molecular information with the micrometer-size features of the chip, and dealing with the errors. The inevitable errors that will be present as computing energies are decreased to $\sim 50 kT$ (where k is Boltzmann's constant and T is temperature) per decision (rather than the present $\sim 10^6 kT$) need not, in principle, cause errors in the overall computation done by such devices.

All the above problems can be addressed by using molecular electron-transfer reactions as the fundamental computing element (8). These reactions (9) are desirable because they involve no bond formation or breakage, are reversible, have tunable rates, have an intrinsic directionality and a natural means of connecting the clock with the energy source [that is, a light pulse (4)]. Figure 1 shows two strategies for constructing a shift register from a chain of electron-transfer active species. These strategies utilize a polymer consisting of three molecular groups (α , β , and γ) per repeat unit. The first repeat unit in the chain is in contact with an electrode. A "1" (or "0") is written by reducing (or not reducing) that unit. Exposing the chain to short intense bursts of light shifts the written state one repeat unit to the right, provided that the processes indicated with solid arrows are much faster than the competing processes indicated with dashed arrows. The potential of the elec-

Fig. 1. (Top) The orbital energy levels in three repeat units of an electron-transfer, shift-register scheme are shown, where the electron shift is initiated by excitation of the donor (α). The presence of a "1" in the second cell is represented by the presence of the electron (small up arrow). The dotted arrow represents excitation of the donor by light. Solid arrows show the transfer reactions which shift the electron one unit down the chain following photoexcitation. Back reactions which decrease the efficiency of the device are shown with dashed arrows. A possible molecular implementation of the monomer in this scheme is shown in Fig. 2 (top). **(Bottom)** Here, the intermediate (β) is excited on every unit of the chain every clock cycle. Units written with a "0" simply relax to the ground state. Proper shifting of the "1" (a hole on site α), written in the central cell in this example, follows excitation providing $k_2 \gg k_{-1}$ and $k_3 \gg k_{-2}$. Transfer from β to α is only allowed when α is vacant. In this case holes are read and written. They travel from left to right. Figure 2 (bottom) shows the monomer for a possible molecular implementation of this scheme. Both strategies in this figure could be equivalently implemented with either chiefly filled or chiefly vacant orbitals.



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trode determines whether a "1" or "0" is written into the shift register during a given light flash. On the three repeat units shown in Fig. 1, the charge state represents the string "010." This design uses periodic light pulses both to provide the power and to be the synchronizing clock signal. Electrons are collected at an electrode at the terminus of the chain. The implementation of this idea requires a polymer with the repeat unit $\alpha\beta\gamma$, in which electrons can be unidirectionally moved one repeat unit per light flash.

A group of 5000 oriented chains of 600 repeat units would be assembled between electrodes (by means of appropriate silyl reagents at the ends of the polymer to covalently link the polymer ends to the electrodes). A total of 600 repeat units would provide chains of 1.2 μm (distance measured along the backbone) assuming that each repeat unit is 20 Å. If there are exactly 600 units in each polymer, the precision of manufacture is absolute, although the precision of the electrode lithography is only ± 1000 Å. The problem of electron transfer between chains is expected to be small because the electron-transfer steps require electron tunneling, the rate of which decreases exponentially with distance. The mean interchain distances are longer than the intrachain distances, and close approach of chains can be prevented by including

bulky groups on the chain. In operation, the material would be immersed in electrolyte to keep the Debye length to ~ 20 Å. The system of 5000 parallel chains, each having the same information stored, is used to allow detection of the electrons at the receiving electrode without further amplification (10). This redundancy also serves the purpose of preserving the written information if some fraction of the chains is degraded or does not transfer the electrons at the proper moment. A probability for excitation and electron transfer of $\geq 99.9\%$ per cycle is required so that at least half of the electrons arrive at the 600th site at the correct time. To achieve this with a donor having an extinction coefficient of $10^5 \text{ M}^{-1} \text{ cm}^{-1}$, a minimal energy flux of 20 mJ/cm^2 per pulse is needed. A 1-cm^2 chip with a 1-MHz clock speed that stores 10^9 bits dissipates only about 1.5 watts because the electron-transfer material is optically thin. The 99.9% efficiency requirement per cycle can be approached by lengthening the duration of the light pulse (see below). Also, writing the information only every other clock cycle will eliminate the possibility of bottlenecks in the pathway at cell connections (8) but will decrease the information density by one-half.

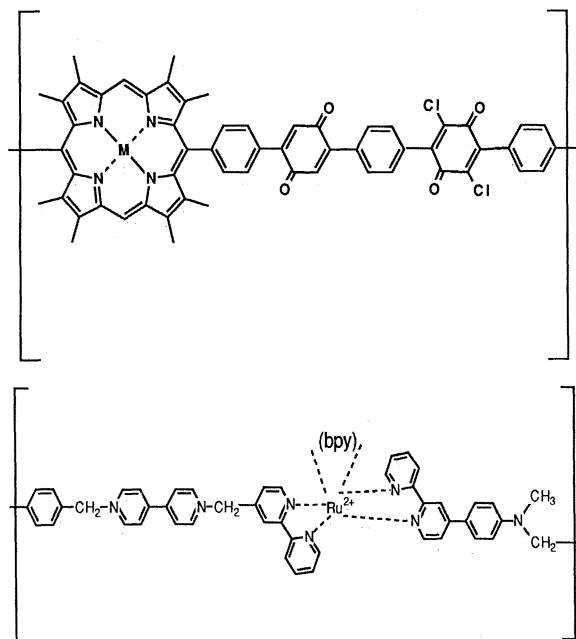
The generic requirements for proper function in systems like the one in Fig. 1 (top)

include: (i) forward transfer from the excited donor must be much faster than the corresponding radiative plus nonradiative decay to the donor ground state ($k_1 \gg k_d$); (ii) all forward transfers must be faster than reverse transfers ($k_2 \gg k_{-1}$) and ($k_3 \gg k_{-2}$); (iii) electron transfer from the excited donor on the site to the right (k_1) must be much faster than the recombination rate (k_{-2}) to avoid a bottleneck at the connection between cells. (Similar systems with more intermediate states might also be used.) The intermediate serves the vital function of allowing a first extremely fast charge transfer to compete with unproductive donor excited state decay. The residence of the electron at the intermediate prevents the confusion of the electron "bits" in adjacent cells. This intermediate also provides a large distance between the acceptor and donor states within a single repeat unit. Because electron-transfer reactions decay approximately exponentially with distance, intermediates are essential for efficient charge transfer over long distances. The intermediate electronic state is chosen with properties such that it does not provide a thermodynamically allowed reverse electron-transfer reaction to occur. "Intermediates" that do not provide real reduced intermediate states, but serve to increase the electronic coupling between two other species, may also prove useful (11). Implicit in this discussion is the need for the clock-cycle time to be long compared to the time required to transfer an electron from donor to donor. Also, the duration of the light pulse must be short enough that the possibility of charge shifts longer than one repeat unit is eliminated. Figure 1 (bottom) shows an alternative scheme with requirements discussed in the figure caption. Figure 2 shows possible implementations of these two schemes.

The three characteristic time-scales in the shift-register polymer system are the time required for charge separation within a monomer unit (τ_c), the time that the charge separated state lives in the isolated monomer (τ_r), and the time to shift the electron one monomer unit down the chain (τ_s). τ_s must be much shorter than τ_r for the chain to function efficiently. τ_s can, however, be made longer than τ_c . The excitation light can then be left on for a time roughly of the order (but less than) τ_s . For illumination time of the order τ_s , each electron will have roughly τ_s/τ_c "chances" to achieve charge separation within a given polymer unit. This relaxes the 99.9% efficiency requirement. For example, a donor having three "chances" to transfer, each with a 90% likelihood of success, fulfills the efficiency requirement.

The directionality of electron or hole transport is provided by the combination of

Fig. 2. (Top) A polymer conforming to the energy level scheme in Fig. 1 (top) is shown ($M = \text{Zn}$ or Pd , for example). The synthesis of such a molecule could follow the strategy developed for the systems in (20) and (21) by using known technology. The polymer would be put into the active state (000...0) by electrochemical oxidation of all porphyrin species; a "1" would be written on the left side of the molecule by reducing the ring. The rates of electron transfer could be tuned by varying the substituents on the porphyrin or quinones, or by changing the bridging groups. Building the porphyrin from functionalized segments (20) would provide a natural means of making this polymer. **(Bottom)** A polymer based on the chromophores used in solar energy conversion schemes could be assembled to conform to the strategy of Fig. 1 (bottom). The polymer does not put any of the chromophores in unusual configurations. The most desirable means of polymerization is less clear than in Fig. 2 (top). The polymer would be put into the active state (000...0) by reducing all methyl viologen species; a "1" would be written on the left side of the molecule by oxidizing the methyl viologen. (bpy) is 2,2'-bipyridine. Methyl viologen is chosen because of its known bimolecular quenching characteristics. A more rigid viologen could probably be used. As in Fig. 2 (top), the rate can be tuned by adjusting the substituents on the redox sites or by altering the bridge. Some unwanted photochemistry may occur in this particular system (because of either excited-state oxidation of species by the metal or double reduction of the viologen). This may be avoided by "tuning" the orbital energy levels of the chromophores through chemical modification to their structure.



energetic, distance, and vibronic coupling effects (9, 15). An electron shift of one repeat unit in the schemes shown in the figures requires three exothermic electron-transfer reactions. The net free-energy change of the shift is zero; the energy of the absorbed photon is fully degraded to heat to achieve the electron transfer. Control of the directionality is achieved by way of vibronic coupling in Fig. 2 (top) (so that the α_i to β_i transfer rate is much faster than the α_i to γ_{i-1} rate) but is achieved by distance constraints in Fig. 2 (bottom). Addition of a spacer (another phenyl ring, for example) between α and γ of neighboring units in Fig. 2 (top) could further enhance the directionality.

Bacterial photosynthetic reaction centers consist of four charge localization sites, cytochrome c, bacterial chlorophyll dimer (Chl_2), bacterial pheophytin (Phe), and ubiquinone (UQ). The overall quantum yield for charge separation in this system (from cytochrome to UQ following Chl_2 excitation) is >95%. The yield of $\text{Chl}_2^+/\text{UQ}^-$ is more relevant to the three-site model described here, but has not been measured directly with much precision. It can be estimated to be 98.9% from the ratio of the Chl^+Phe^- recombination rate to the rate of Phe^- to UQ electron transfer (12–14). Thus, synthetic structures in the style of the reaction center and having quantum efficiencies >99% are expected to be possible.

Purely organic or organometallic charge-localizing species might be used to build these shift memories. The basic constraints on the molecular systems are: (i) low vibronic coupling to decrease the rate of back reactions; (ii) rigid linking structures so that molecules are unlikely to fold back on themselves; (iii) good covalent linking pathways between groups; (iv) choice of groups so that dimerization of strands is unlikely and interchain electron transfer is not possible; (v) resistance to photodegradation; (vi) appropriate redox levels; (vii) availability of condensable monomer units or a scheme to add groups serially. This molecular design problem is certainly solvable, though not easy, within the current framework of chemical synthesis and electron-transfer theory (15, 16). Examples of "prospective" systems are shown in Fig. 2 based on the schemes in Fig. 1.

Schemes to build the materials could adopt four basic strategies. One would use known organic synthetic schemes to build up the chains. For example, ring opening polymerization of olefins (17) might be used to form a rigid conjugated backbone with appropriate pendant groups. Rigid-rod molecules and polymers are known and could be modified to include useful chromo-

phores (18). Organic polymers containing pendant metal complexes, some electron transfer-active, are also known (19). The challenge of these materials would be to make chains having several different metal environments. A second scheme to create the polymers would involve the linking together of multisite photosynthetic (small molecule) model compounds (20, 21). A third scheme would take advantage of the linear structure of DNA to which sequence-specific chromophore-bearing groups could be bound (22–24). A fourth strategy would use ordered multilayer assemblies of chromophores such as Langmuir-Blodgett films. Two-component films have recently been made and shown to be electron transfer-active (25).

Consideration of this shift register and its weaknesses focuses attention on several significant aspects of molecular computation. For instance, although computation based on molecular devices might reasonably promise computation energies of $\sim 50\text{ kT}$ per bit handled, the present chip design needs about $5 \times 10^5\text{ kT}$ per bit handled. The fundamental origin of this ineffectiveness is the unbranched structure of the polymer. The need for 5000 electrons at the chain end necessitates 5000 strands everywhere. If, however, a molecular branch unit could be made so that one electron arriving at a fork could generate two electrons and a hole traveling on separate strands, one electron could be amplified into 1000 in ten branchings. Such a scheme would reduce the energy per bit to 1000 kT . Forks, and the ability to copy information rather than merely move it, are also essential to more complex computations and computational devices. Controlled forks would be even more useful.

If digital computation is to be carried out at a molecular level, a "bit" must have a physical representation. Possibilities include the presence or absence of an electron, an electronically excited state, an exciton, a soliton, a spin, a molecular configuration, and so forth. The choice made here of an electron has the advantage that it interfaces in a natural way with reading and writing by electrical circuits. In addition, the conservation of electrons tends to keep bits from being spontaneously created or destroyed. There are also well-developed ways to move electron "bits." The absence of a well-developed "copy" procedure is a weakness shared by all the possible "bit" representations.

A three site per repeat unit photoinduced shift polymer would be interesting in its own right. The general question of light-driven shift polymers can be investigated with short oligomers tethered at only one end, and without the need for microfabrica-

tion. The materials science and chemical synthesis questions raised in such schemes are also of interest for more conventional electronics. For example, much simpler electron-transfer polymers could be made to serve as "molecular wires" over short distances in conventional VLSI without the need for light as a driving source. This would be particularly attractive if a class of specific surface to polymer end bindings which would enforce appropriate self-assembly were developed (26). Such an approach relates particularly to neural network chip architectures, where the connectivity is complex, where wiring faults can be tolerated, and for which connections having a large resistance can be a central part of a complicated circuit.

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Simulation of Eolian Saltation

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Saltation is important in the transport of sand-sized granular material by wind and in the ejection of dust from the bed both on Earth and on Mars. The evolution of the saltating population and all its characteristic profiles is calculated from inception by pure aerodynamic entrainment through to steady state. Results of numerical simulations of single-grain impacts into granular beds are condensed into analytic expressions for the number and speeds of grains rebounding or ejected (splashed) from the bed. A model is combined with (i) this numerical representation, (ii) an expression for the aerodynamic entrainment rate, and (iii) the modification of the wind velocity profile by saltating grains. Calculated steady state mass fluxes are within the range of mass fluxes measured in wind tunnel experiments; mass flux is nonlinearly dependent on the shear velocity. Aerodynamically entrained grains in the system are primarily seeding agents; at steady state, aerodynamic entrainment is rare. The time for the entire system to reach steady state is roughly 1 second, or several long-trajectory hop times.

SALTATION IS THE PRIMARY MEANS BY which sand-sized particles travel in most realistic winds (1). In pure saltation, particles travel smooth paths that are essentially unaffected by turbulent fluctuations of the wind between periodic encounters with the bed; as grain size decreases or wind velocity increases, saltation grades into pure suspension (2, 3), where turbulent fluctuations dominate the trajectories. Understanding the physics of blown sand is necessary for accurate prediction of sediment transport on Mars (4) and soil loss due to wind erosion (5), for understanding the origin of such geomorphic features as ventifacts (6) and ripples (7, 8), and for reconstruction of environmental conditions from the eolian rock record (9, 10). Wind tunnel saltation experiments (4, 11, 12) have led to empirical relations between the total mass flux and a characteristic wind velocity, typically chosen to be the shear velocity, u_* (13). Profiles of mass flux, $q_m(z)$, and concentration, $c(z)$, decay monotonically and sharply above the bed both in blowing snow (14) and in blowing sand (4, 11, 12). In addition, natural obstacles have erosion profiles that indicate a distinct maximum in abrasion above the bed (15, 16); such profiles con-

strain the pattern of kinetic-energy flux to the obstacle (6).

Earlier workers (1, 3, 17, 18) recognized that the initial launch velocities (speed and angle) of grains ejected from the bed are diverse. They used the various profile data to constrain the probability distribution of these velocities. Grain trajectories were integrated forward in time and mass flux and concentration were calculated as each trajectory passed first upward, then downward through a particular height element. Each trajectory and the resulting mass flux and concentration profiles were then weighted according to a chosen probability distribution, the parameters of which were altered

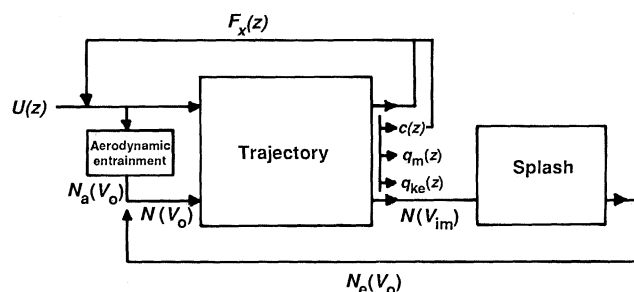
until a match was achieved with an appropriate empirically derived profile. Importantly, these matches required a knowledge of the total number of grains in saltation. Typically, the total calculated mass flux was forced to obey an empirically derived relation to the shear velocity (that is, the mass-flux "law") (3). In these models the preponderance of grains travel in low-speed, near-bed trajectories; the highest liftoff speeds are the least likely, as observed in nature.

Although the models calibrated for mass flux yielded reasonable concentration and kinetic-energy flux profiles (6), they had several severe deficiencies. Reliance on a mass-flux law to set the total number of grains in saltation precluded insight into how the mass flux and the probability distribution of the initial velocities emerged from the physics of the problem. The models were also unable to provide information about the shape of the wind velocity profile. In addition, because nothing was learned about the time scales involved in the approach to steady state saltation (the calibrations were with steady state wind tunnel data), no foundation was laid for the treatment of the more complex case of a variable wind.

Many of the deficiencies of these models can be removed by incorporating the physics of (i) the grain-bed interaction and (ii) the feedback involved in the extraction of momentum from the wind by the accelerating grains (Fig. 1). The grain-bed interaction sets the probability distribution of the initial conditions, and the wind velocity alteration is responsible for eventually limiting the total number of grains in transport. (The energy in the wind is the limiting resource available for the growth of the saltation population.)

We performed numerical simulations of single-grain impacts into a granular bed to evaluate quantitatively the splash process.

Fig. 1. Schematic diagram of the processes involved in the eolian saltation system. Initial wind velocity profile, $U(z)$, sets aerodynamic entrainment rate, $N_a(V_0)$, in grains per unit area per unit time being ejected from the bed with the lowest possible velocity ($V_{0\min}$). Grain trajectories are calculated, resulting in profiles of concentration, $c(z)$, mass flux, $q_m(z)$, kinetic energy flux, $q_{ke}(z)$, and horizontal force on the wind, $F_x(z)$, as well as the impact velocities of each grain trajectory, V_{im} . The grain splash is calculated for each impact according to a probabilistic description (26), resulting in a new number of ejecta, $N_e(V_0)$ (including both rebounding and splashed grains), in each of the initial velocity "bins." At each time step the wind velocity profile is modified according to the imposed force profile, resulting in a new shear stress at the bed and a corresponding change in the aerodynamic entrainment rate. The new splash ejecta are added to the new aerodynamically entrained grains to produce the total number of grains leaving the bed at the next step, $N(V_0)$, and the calculation is repeated until a steady state is achieved.



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