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Controlled Electron Transfer for Molecular Electronics

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Controlled Electron Transfer for Molecular Electronics

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The ability to flexibly initiate and control electron transfer reactions in molecules contributes to their central role in molecular electronics. Conventional applications of electron transfer reactions discussed in this volume center on organic conductors and chromophores for nonlinear optics. However, molecules that undergo thermal or photoinduced electron transfer might serve as the basis for very small scale electronic devices. We will present a summary of our proposal for a shift register memory based on electron transfer reactions, and the synthetic tools that are needed to implement the proposal. A unique function of biomolecules is derived from their ability to deliver electrons to *specific* sites in proteins at prescribed rates. An understanding of how biology solves the rate control and selectivity problem may aid the design of semi-synthetic systems for molecular electronic applications. We will describe a scheme for mapping the specific bonds within proteins that mediate the donor-acceptor coupling responsible for distant (> 10 Å) electron transfer.

I. CONTROLLING ELECTRON TRANSFER FOR MOLECULAR ELECTRONICS

One goal of molecular electronics is to supply computational elements which exploit the molecular rather than bulk properties of materials.[1] Using molecular properties should allow the design of the devices from small up, and tuning of their properties with molecular modifications.[1c] In spite of the fascinating variety of molecules that have been proposed as molecular devices, insufficient emphasis has been placed on molecules that are synthetically tractable and could exploit molecular sizes using known physical chemistry. Synthetically tractable means that the molecules could be assembled using known synthetic techniques. They must derive their function from well known physical chemistry, allowing them to perform in a manner that can be modified by making routine synthetic changes to the molecules. To exploit molecular sizes, relatively few large size (micrometer or larger) elements should be needed to operate the device per molecular functional element.

Five challenges must be addressed in the design of a molecular electronic device: delivery of the energy at the molecular level, delivery of the clock signal to the device, interconnection of the molecular devices, communication between the macroscopic world and the molecular device, and dealing with errors.

Molecule-size devices are appealing because of their potentially large device density and low energy consumption. Many nanometer-size molecular features are needed per larger (micron size) interconnection with the macroscopic device if a net benefit from the molecular dimensions is to be realized. Another difficult problem is associated with interfacing single molecules with larger features. In the device described below, we circumvent the specificity problem (and error correction problems) by operating many molecular devices in parallel.

Molecule scale information could be written or processed in a few ways. Molecular conformations, bonding, charge distributions, or oxidation states, for example, could be used as information carriers. Because of the ease of writing, shifting, and detecting electrons, particularly with the assistance of light, we have focused on a molecular device based on electron transfer reactions.[1,2]

We begin with a brief summary of how to modify the rates of electron transfer between donor and acceptor. We then describe the design of a molecular shift register memory[3] based on electron transport reactions that should be capable of information storage densities considerably larger (100–1000 times) than currently available. The device could consume up to 10,000 times less energy than conventional VLSI devices if implemented in conjunction with a molecular charge amplifier, although the design of a molecule scale charge amplification is also a current conceptual challenge.[3] We will also discuss strategies for assembling the device. Finally, we will discuss new methods for predicting the rate of electron transfer reactions in biomaterials.

Electron transport between two localized electronic states can be controlled by modifying the electronic coupling (tunneling matrix element), the nature of the nuclear modes coupled to the two electronic states (Franck-Condon factor), and the coupling between electronic and nuclear motion. For weak donor-acceptor coupling, the reaction is generally nonadiabatic and both electronic and nuclear factors make exponential contributions to the rate (electronic couplings decay exponentially with the donor-acceptor separation—typical decay length scale of 1 Å—and the nuclear term is exponential in the activation energy—typical energy scale of < 1 eV). These parameters are sufficiently adjustable to allow tuning of electron transfer rates from the second to the picosecond domain.[4] The photosynthetic reaction center is an example of a system that exploits this variability of rates to achieve high efficiency. The rate tunability makes electron transfer reactions a convenient foundation on which to base molecular scale electronic devices.

In the covalently bound compounds with relatively large donor-acceptor separations of interest here, the electronic coupling is mediated by the bridging orbitals; direct donor-acceptor interaction is weak. The interaction can be modified by (1) changing the energetics of the donor and acceptor electronic states relative to the bridging orbital levels, (2) changing the topology of the bridge, or (3) changing the length of the bridge.[5] Drastically changing the electronic structure of the bridge (e.g. changing atom type or hybridization) can cause large changes in the coupling. Our understanding of these effects, combined with information about donor-acceptor model compounds, is sufficient to allow the rough theoretical design of donor-acceptor pairs with prescribed electron transfer rates.

II. THE MOLECULAR SHIFT REGISTER

A shift register is a form of memory with the memory elements connected in a line. Information is written at the left terminal cell during each clock cycle, and the contents of each cell are shifted one unit down the chain to the right. One bit of information is also read out at the right terminal cell (Figure 1). Some conventional memories and information delay lines are based on shift register strategies (magnetic bubble memories are shift registers). The shift register described here relies on molecular electron transfer reactions. Proof of concept structures are planned which take advantage of the tunability in the rates of electron transfer. The synthetic strategy is based on designing somewhat modular and interchangeable electron transfer species since rates are more easily tuned with the help of theory than predicted in an absolute sense. We hope that this strategy will lead to the development of other kinds of molecular devices based on "interchangeable parts."

A linear chain of DA molecules would form a shift register memory element as shown in Figure 2. The electron shifting sequence would be initiated in those cells containing an electron ("1") on D by a global light flash of the proper wavelength to excite the D to D* electronic transition. A "1" (or "0") in each cell is indicated by the presence (or absence) of an electron on D prior to the flash. The electron transfer within a cell occurs from D* to A followed by the shift of the charge to the next cell to the right. Information which is written on the left side of the chain (one bit at a time) advances down the chain one unit per clock cycle (light flash). Figure 2 shows the arrangement of donor and acceptor levels which form the basic skeleton of a molecular shift register.

This scheme of coupled electron transfer units satisfies the device design requirements presented above: the energy is provided by light; the clock signal is provided by pulsing the light; the chemistry for linking donors and acceptors is known[4,6]; interconnections with silicon may be provided by appropriate surface binding groups; errors can be dealt with to some degree with multiple chains or

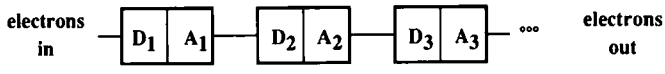


FIGURE 1a The general shift register scheme is shown.

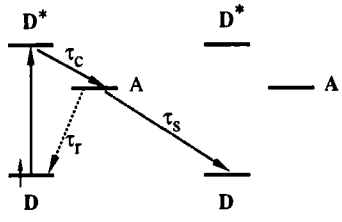


FIGURE 2 The important time scales for the shift register are shown: charge separation within a cell (τ_c), charge recombination within a cell (τ_r) and charge shifting between cells (τ_S).

other methods. Information is written and read at electrodes bound to the first and last groups of the polymer respectively.[3]

The internal details of each unit will be more complicated than suggested in Figure 2 (see Figure 3 below). Figure 2 shows the three characteristic time-scales of the system. These times are: the change separation time within a single unit (τ_c), the charge separated lifetime in an isolated monomer (τ_r), and the charge shift time between cells (τ_s). Monomer units with appropriate rates would be roughly 20 Å in length. Interfacing with micron scale architecture, then, would require chains of about 600 repeat units (bits) or longer. Chains comprised of these units would be bound between two electrodes on a VLSI substrate[3] and immersed (or imbedded) in electrolyte to maintain a Debye length of roughly 20 Å. To simplify detection of the arriving electrons and minimize error problems, roughly 5000 identical chains would be needed between the electrodes. The active elements of the memory device would fill roughly one square micron. Smaller numbers of molecules could be used, but then the signal would require external amplification. Implementations which include strategies for molecular level charge amplification and error correction could reduce the number of chains needed. In such a case the energy consumption per bit processed would approach the molecular scale energy, orders of magnitude smaller than the energy consumed per bit processed in conventional devices. The efficiency of transfer between cells must be greater than 99.9% so that half of the written electrons arrive at the reading electrode after 600

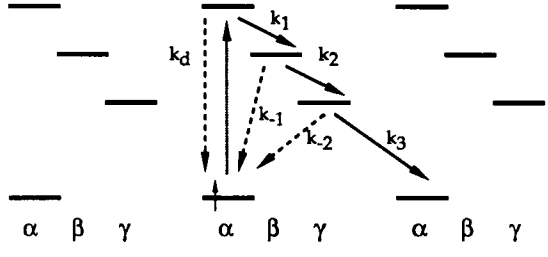


FIGURE 3a The energy level scheme for a shift register based on electron information carriers is shown.

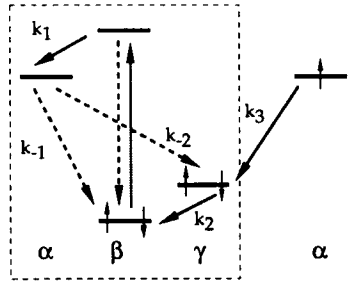


FIGURE 3b The energy level scheme for a shift register based on "hole" information carriers.

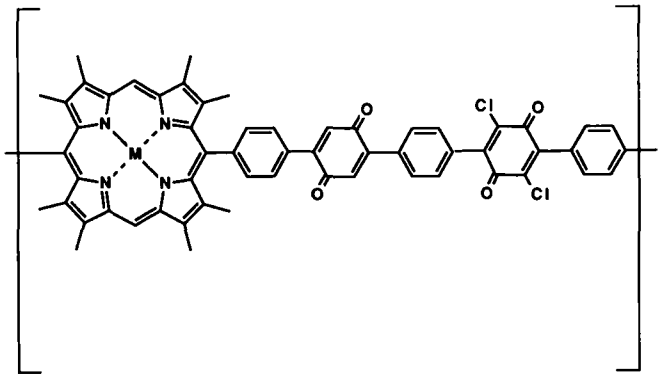


FIGURE 3c A possible molecular implementation of the scheme in 3a.

cycles. Photosynthetic systems suggest that such efficiency can be achievable in tailored electron transport systems.[4] In addition to chemically optimizing the forward transfer rates, strategies which give the electrons several chances to transfer are possible. The 99.9% requirement can probably be satisfied in real systems by manipulating the duration of the excitation pulse. Pulses must be shorter than τ_s to avoid multiple electron shifts during a single flash. Pulses of length $\tau < \tau_s$ provide roughly τ/τ_c "chances" for the desired electron transfer. If the donor is excited three times, with a 90% chance of electron transfer per excitation, the 99.9% efficiency constraint is satisfied. Cells which utilize multiple wavelength excitation schemes or which allow for some form of periodic information restoration might also be used to increase efficiency.[3]

III. SHIFT REGISTER IMPLEMENTATIONS

We now present orbital energy level schemes and a molecule which could provide proper shifting of information. In the first scheme, Figure 3a, bits are written as electrons which move from left to right. Three charge localization sites per unit provide adjustability in the separation and recombination rates as well as enhanced efficiency. The second example (Figure 3b) writes the bits as "holes" which move from left to right and the system is driven by excitation of the central group of the repeat unit. Other implementations are also possible.[3] Obvious problems in construction of the device include: (1) development of a flexible synthesis for the repeat unit, (2) oligomerization or polymerization of that unit to form a processable material, and (3) attachment of that molecule with proper orientation between the two electrodes. Progress in this field will probably begin with a proof of concept that electrons in a single molecule can be induced to undergo stepwise motion through the molecule, one step per light flash. Once established, work on oligomerization and surface attachment can proceed. The molecule shown in Figure 3c

is meant as an illustration of the type of system suggested by the scheme in Figure 3a. Other energy level schemes and backbone supports may be more desirable.

IV. ELECTRON TUNNELING PATHWAYS IN PROTEINS

Biomolecules are appealing ingredients for molecular electronic devices. The reasons include their efficiency in undergoing certain electronic or conformational transitions and the prospects for their self-assembly or organization. One can imagine, for example, attempting to assemble the shift registers described above (and other devices) from biological components.

Electron transport reactions are ubiquitious in biological systems. Photosynthetic reactions in plants, and the respiratory pathways in animals, involve electron transport. We recently developed a model for calculating the dependence of the donor-acceptor coupling and transfer rate on bridge structure in small molecules and proteins,[5,7] Refinements continue to be added, but the model in its present form provides a framework for the interpretation of existing experimental systems and the design of new ones. The theoretical challenge is to understand the dependence of the transfer rate on structural details of the intervening covalent protein.

To focus the discussion, it is useful to introduce the concept of a *physical tunneling pathway*. A physical pathway is defined as a collection of interacting covalent bonds in the medium around and between the donor and acceptor which make some contribution to the net donor-acceptor interaction. One expects a relatively small number of pathways to contribute to the interaction due to the inhomogeneity of the protein medium and the rapid decay of the interaction with the number of bonds on the tunneling path. Either exact or perturbation theory methods (for a given hamiltonian) can be used to calculate the coupling arising from one physical pathway. Interactions between pathways may be important, particularly when there is a large number of physical pathways of comparable length (preliminary results indicate that conclusions can in fact be drawn from the relatively few "dominant" pathways). Because of the rapid decay of the interaction, most strategies write the decay of the donor-acceptor coupling as a product of decays per bond (or delocalized group),[5b] as given in Equation 1. Using perturbation theory, the per bond decay is shown to depend only on the tunneling energy and the nature of the particular bonds in the pathway. Applying this method to lowest order neglects scattering corrections to the wave function propagation in the protein bridge. These corrections for a given pathway arise from enumerations of bonds longer than the shortest path from donor to acceptor. A physical pathway consisting of bonds 1, 2, 3, 4, . . ., for example, has the direct pathway 1-2-3-4 . . . and the scattering pathways 1-2-3-2-3-4 . . ., etc. Scattering pathways can be included in the calculation by correcting the self energy or each orbital on the path.[8] Such methods also write the coupling as a product and sum up the scattering corrections. Summing contributions from multiple pathways is somewhat more complicated, but can also be done.

Our goal is to estimate the donor-acceptor electronic coupling for specific proteins

to define dominant pathways. The rate of transfer is proportional to the square of this coupling for weakly interacting donor-acceptor systems. The coupling for a single physical pathway is[5,8]

$$t_{DA} = prefactor \prod_{i=1}^{N} \epsilon_i \tag{1}$$

and neglecting interactions between pathways, the overall coupling is a sum over t_{DA}'s for all physical pathways (assuming noninteracting pathways). Along a pathway, ϵ_i for each group can be calculated approximately or exactly.[5,8] The prefactor depends on the donor (acceptor) interactions with the first (last) bond of the pathway. Rate differences between experimental systems with similar (or properly scaled) prefactors and nuclear factors are expected to result from differences in the coupling via particular pathways.

We identify the decays, ϵ_i, as occurring either through bond (between two covalent bonds sharing a common atom, or between two hydrogen bonded groups) or through space (between unbonded groups).[5] The decay factors associated with these interactions are respectively ϵ_B, ϵ_H, and ϵ_S. In a one-electron tight-binding model the perturbation theory value of ϵ_B is

$$\epsilon_i = \frac{\beta_i \gamma_i}{(E - \alpha_L^i)(E - \alpha_R^i) - \beta_i^2} \tag{2a}$$

where β_i is the resonance integral between hybrid orbitals in bond i and γ_i is the resonance integral between bonds connected to the same atom. α_L^i and α_R^i are the site energies of the two orbitals in the i^{th} bond. To emphasize the role played by hole and/or electron tunneling (mediation via the bonding or antibonding protein levels, respectively), ϵ_i can be rewritten

$$\epsilon_i = \epsilon_e + \epsilon_h = -\frac{\gamma_{12}^{eff}}{E - E_a^{(2)}} + \frac{\gamma_{12}^{eff}}{E - E_b^{(2)}}. \tag{2b}$$

E_a (E_b) is the antibonding (bonding) orbital energy of bond i.

A family of protein bridged electron transfer systems is now emerging which has (not necessary physiological) donors and acceptors at fixed and known distances. These proteins have surface histidines labeled with a ruthenium complex. To survey tunneling pathways, we have made the assumptions:

$$\epsilon_B = const. \times \exp[-\beta_0(R - R_{eq}^B)] \tag{3a}$$

$$\epsilon_S = \sigma_S \bar{\epsilon}_B \, exp[-\beta_1(R - R_{eq}^B)] \tag{3b}$$

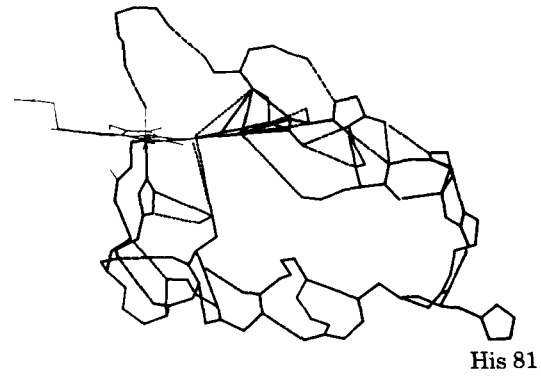
$$\epsilon_H = \sigma_H \bar{\epsilon}_B^2 \, exp[-\beta_2(R - R_{eq}^H)] \tag{3c}$$

$\bar{\epsilon}_B$ is the value of ϵ_B for an equilibrium length bond, ~0.4 − 0.6, and used a tree-like search strategy to find important pathways.[5d] The β factors define the distance dependence of the interactions and the σ factors specify their orientation dependence. In practice, we choose $\sigma_H = 1.0$, $\sigma_S = 0.0 - 1.0$, $\beta_0 = \beta_1 = \beta_2 = 1.0 - 1.7$ Å^{-1} and *const.* = 0.6 for pathway surveys (three parameters). The σ values can be varied to determine pathways which exclude through space or hydrogen bonded segments. These expressions result from theoretical and experimental analysis of protein mediated electron transfer. Especially important is the theoretical prediction of the cental role played by the hydrogen bonds which link up covalent pathway segments. This method maps out the dominant tunneling pathways and should assist in protein design. In fact the method has even predicted rate differences between isomers of cytochrome *c* with similar transfer distances but rather different transfer rates. Reference 5 describes this work in detail, correlation between the experimental and theoretical couplings, and uses of the model for protein design. Figure 4 shows the kinds of tunneling pathways which have been identified in the ruthenium labeled derivatives of myoglobin which were synthesized in the Gray laboratory.[9] Figure 4a shows the importance of protein α-helix for mediating coupling in the Ru(His81) myoglobin derivative. Figure 4b, shows, in the Ru(His12) myoglobin derivative, how pathways can utilize small segments of α-helix linked together with through space contacts in order to minimize the overall path length (i.e. maximize the coupling).

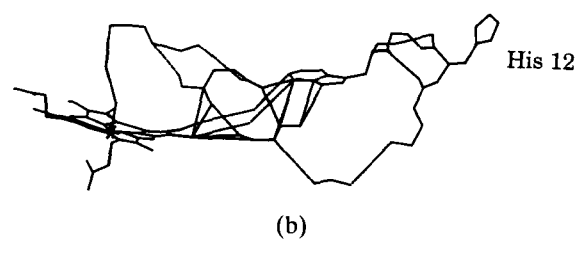
These methods of mapping tunneling pathways are leading to an understanding of electron transfer in complicated biomaterials and the design of materials with prescribed electron transfer rates.[9,7]

VI. CONCLUSIONS

We have argued that electron transfer reactions, by virtue of their tunability, occurrence in efficient natural systems, and suitability for detailed theoretical analysis may form the basis for future molecular devices. A target molecular device, the shift register, was presented as a challenge to synthetic chemists. Synthesis of multi-site charge localizing species, i.e. proof of concept molecules, could lead to the eventual synthesis of devices with functional units on the molecular scale. While the synthesis and interfacing of the macromolecules will undoubtedly prove quite challenging, the physical chemistry upon which the device would function is well established. The potential role for biomolecules in molecular electronics was described in several of the papers in this volume. Those systems which employ electron transfer within or between the biomolecules will have transport rates dependent on the details of the biomolecular electronic structure. We have developed a method of mapping out the important residues in the protein which are responsible for mediating the donor-acceptor interactions in these proteins. So far, the method is consistent with the family of data available for ruthenated heme proteins,[5d] and is being used to design new materials and to predict the dependence of the rate on details of the protein medium in mutants which are being prepared using site-directed mutagenesis techniques. Hopefully, an ability to predict rates and achieve



(a)



(b)

FIGURE 4 Tunneling pathways in ruthenated myoglobin derivatives.[5,7a]

their real control through amino acid modification in tailored proteins will contribute to the development of bio-molecular electronic devices.

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