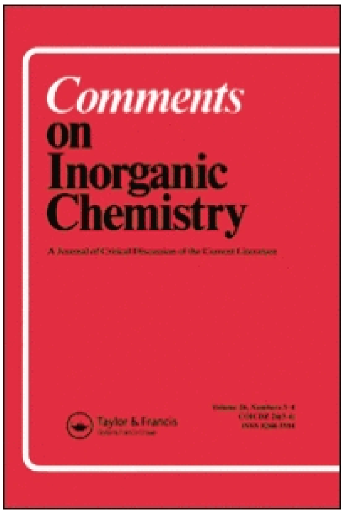

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Prospects for a New Kind of Synthesis: Assembly of Molecular Components to Achieve Functions

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Prospects for a New Kind of Synthesis: Assembly of Molecular Components to Achieve Functions

Molecular scientists now have an opportunity to add an important new dimension to synthesis. Preparation of chemical systems, comprising two or more components, to achieve a function is possible. While rational strategies exist for some simple systems, major advances in fundamental reaction chemistry at the molecular and macromolecular level, especially at interfaces, are required to achieve practically significant synthetic objectives. Synthetic chemical systems inspired by nature and microelectronic devices illustrate some of the aspects of systems synthesis. These example systems include multicomponent catalysts, the photosynthetic apparatus for solar energy conversion, diodes, and transistors.

INTRODUCTION

The aim of this Comment is to raise the consciousness of inorganic chemists to the opportunities associated with the application of molecular science to the preparation of "systems" having functions derived from judicious assembly of molecular components. It can be argued that molecular synthesis has progressed to a point such that molecules of any complexity can be prepared, provided sufficient resources are applied to the problem. The preparation of vitamin B_{12},[1] among other examples, stands as one of the crowning achievements of molecular synthesis. While the synthesis of vitamin B_{12} cannot be regarded as "practical," the synthesis of vitamin B_{12} and numerous other large, structurally complex, natural substances illustrates that the perceptive application of synthetic methodology

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and the continuing development of new, useful synthetic methods allows the conclusion that almost any desired molecule can be prepared. With this assumption, it is thus evident that there exists an opportunity to begin assembling "systems" from synthetic, molecular components.

A large group of inorganic chemists have focused their attention on molecules. Structural characterization of "small" molecules has comprised a major accomplishment in inorganic chemistry, beginning with Werner's classic work on six-coordinate complexes[2] and including pioneering work on metal carbonyls by Hieber,[3] sandwich and other organometallic complexes by Fischer[4] and Wilkinson,[5] metal–metal bonded complexes by Cotton,[6] and models of metal-containing biological molecules by Holm.[7] As for other molecules, the structural characterization of molecules containing metals has led to considerable understanding of reactions, and in many cases rational synthetic methodology has emerged for the preparation of molecules of great structural, chemical, and physical diversity. Elegant molecular synthesis of metal-containing substances has led to the preparation of new classes of materials, practically important catalysts, and molecules that elaborated understanding of electronic structure, bonding, reaction mechanisms, and the function of small molecules in large "systems," especially biological systems.

With the considerable knowledge presently available concerning the synthesis, structure, and reactions of inorganic molecules coupled with the fact that properly assembled molecules, as in natural biological systems, can achieve a function characteristic of the assembly, there exists an opportunity to undertake a new kind of chemical synthesis. The rational preparation of multicomponent chemical "systems" of significant geometrical dimension, up to a few μm, is possible. It is now appropriate to define "system." A chemical system will be taken to be an assembly of at least two components that together yield a function characteristic of assembly. Examples of such systems can be found in nature and in man-contrived electronics. Discrete microelectronic devices provide realistic examples, because their size is sufficiently small (crucial dimensions of 1 μm or less) that there is a realistic possibility that their discrete functions can be duplicated using assemblies of molecules. In practice, instant photography systems developed by Kodak and Polaroid represent modern examples of molecule-based (imaging) systems. Illustrations of the synthesis of chemical systems, and conjecture concerning new ones, are developed below within the framework of duplicating functions of chemical systems found in nature or of discrete microelectronic devices.

CHEMICAL SYSTEMS INSPIRED BY NATURE

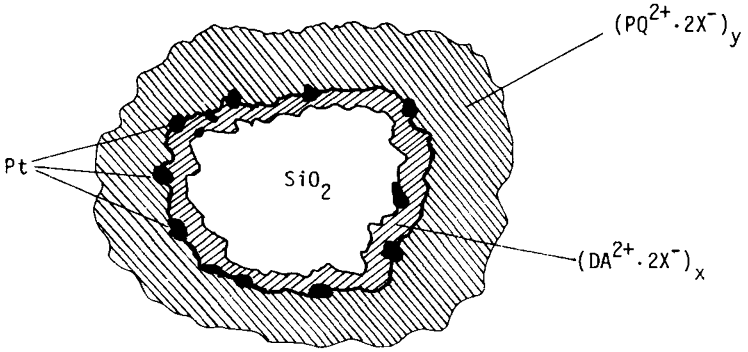
There are many subsystems of a living system that can serve as targets for chemical synthesis. The objective of the synthesis is not necessarily to duplicate *exactly* the natural system, but could be to synthesize a system that will duplicate the *function* of the natural system with components that might be abiologicial. Perhaps the smallest departure from a major theme of modern inorganic chemistry research is the synthesis of multicomponent catalysts. Indeed, in this area systems synthesis would appear to be most straightforwardly understood. Accordingly, this area will be used as one concrete example where accomplishment is readily possible. A second example of an important subsystem in biology is the solar energy conversion apparatus that consists of many molecular components assembled in such a way that photoexcitation of an absorber molecule results in unidirectional electron transfer and, ultimately, the formation of thermodynamically unstable redox products. There are numerous other subsystems of living systems aside from complicated catalysts and solar energy conversion, but these provide ample illustrative value. Successful chemical synthesis of such systems would likely lead to practical return as well as deeper understanding of biological–chemical systems.

Multicomponent Catalytic Systems

Molecular scientists have been very successful in synthesizing useful transition metal complex catalysts that operate under mild conditions to give good product specificity, high yields, and large rates. Excellent illustrations include the Sharpless asymmetric epoxidation catalyst,[8] Bosnitch's asymmetric hydrogenation catalysts,[9] Schrock's alkyne metathesis catalysts,[10] and Collman's catalyst for the $4e^-$ reduction of O_2 to H_2O.[11] As important as such catalysts are, and as important as future efforts will continue to be, these are not examples of chemical systems, since the function is achieved with a single component. Single component function is, of course, crucial to the overall function of a system, but conventional molecular catalysis does not, generally, comprise a chemical system according to the definition above which requires that a system be an assembly of at least two components.

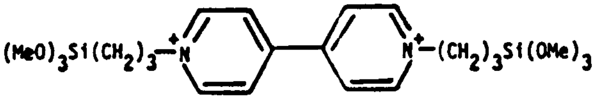
Nature provides many examples of multicomponent catalysts. For example, biological systems appear to routinely catalyze complex, multielectron redox reagents such as O_2 (and a substrate) to product via multicomponent systems. In such cases there often appears to be a site of "activation" or "binding" of the complex redox reagent coupled in some fashion to an apparatus for transferring electrons stepwise to the site. The function of such multicomponent systems might be said to be the interconversion of complex, multielectron (typically inner-sphere), redox reagents and simple, one-electron (typically outer-sphere), redox reagents.

As a modest example of a multicomponent catalyst system consider the system represented by Scheme I.[12] The catalyst, $[SiO_2](DA^{2+} \cdot 2X^- \cdot Pt)_x/(PQ^{2+} \cdot 2X^-)_y$, has the function that it will interconvert the two-electron reductant H_2, in aqueous solution, and a one-electron, outer-sphere reductant of equivalent reducing power. The useful catalysis that can be achieved is the one-electron reduction of large biological redox reagents, such as horseradish peroxidase, that are



SCHEME I A multicomponent catalyst system for the one-electron reduction of biological redox agents using H_2 activation that then results in reduction of the $(PQ^{2+})_n$ polymer coating the "buried" Pt particles. The $(PQ^+)_n$ is capable of reducing large biological redox reagents ordinarily unaffected by H_2 or by Pt surfaces exposed to H_2 (Ref. 12).

generally difficult to reduce at interfaces and are inert to H_2. Notice that the system in Scheme I is structured in such a way that the site for H_2 activation, the Pt, is buried under the $(PQ^{2+} \cdot 2X^-)_y$ polymer derived from I.



I

The small H_2 molecule can diffuse through the outer coating of $(PQ^{2+} \cdot 2X^-)_y$ to the Pt. The $(PQ^{2+} \cdot 2X^-)_y$ polymer is in contact with the Pt particles which activate H_2 in aqueous solution. Thus, reduction of $(PQ^{2+} \cdot 2X^-)_y$ polymer occurs reversibly according to Eq. (1).

$$[SiO_2](DA^{2+} \cdot 2X^- \cdot Pt)_x/(PQ^{2+} \cdot 2X^-)_y + y/2H_2 \rightleftarrows [SiO_2](DA^{2+} \cdot 2X^- \cdot Pt)_x/(PQ^{+} \cdot X^-)_y + yX^- + yH^+ \quad (1)$$

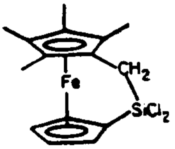
Large biological molecules cannot penetrate to the site of H_2 activation and are thus protected from hydrogenation and hydrogenolysis that might pose complications if the biological reagent were to contact the Pt.

The function of the two-component system represented in Scheme I is to interconvert H_2 and one-electron reductants. In nature this function appears to be achievable with the enzyme hydrogenase[13] which inspired the synthesis of the catalyst in Scheme I. Hydrogenase will catalyze the process represented by Eq. (2), and can be regarded as a single component catalyst.

$$H_2 + 2MV^{2+} \rightleftarrows 2MV^{+} + 2H^{+} \quad (2)$$
$$MV^{2+} \equiv \text{N,N'-dimethyl-4,4'-bipyridinium}$$

The two-component catalyst of Scheme I does what the single-component enzyme does, but the synthetic system of Scheme I operates by a different mechanism.

The two-component system in Scheme I can be extended to a three-component system by anchoring a redox enzyme to the outermost portion of the $(PQ^{2+} \cdot 2X^-)_y$ polymer. It is known that many redox enzymes can be rapidly equilibrated with the $MV^{2+/+}$ solution mediator system.[14] It therefore appears logical to extrapolate the system in Scheme I to a three-component catalyst with the function of effecting catalytic reduction with H_2. Such a system has credibility, because it is known that immobilization of enzymes onto polymers is possible, and can lead to better enzyme durability.[15] Judicious assembly of noble metals, redox polymers, and enzymes makes possible many complicated catalytic processes. The idea could be extended to include oxidation with O_2. For example, SiO_2 microspheres could be modified with Ru/RuO_2 followed by derivatization with a ferrocene-based polymer, such as one derived from hydrolysis of reagent **II**,[16] and capped with a redox enzyme.

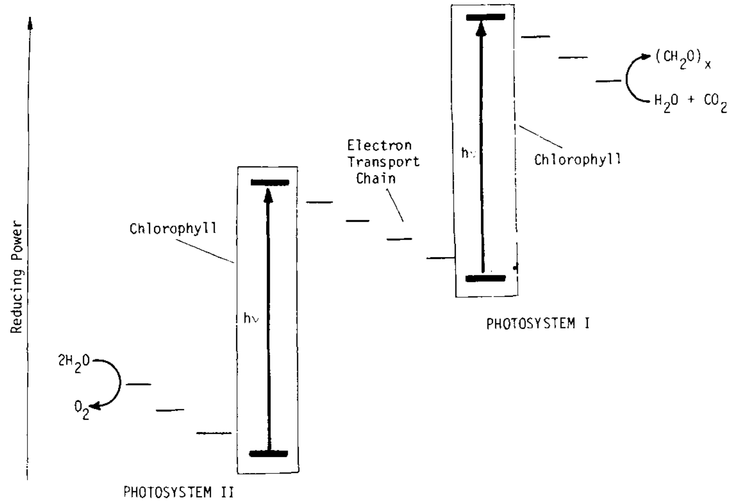


II

The Ru/RuO_2 should activate O_2 [17] which results in the oxidation of the ferrocene-based polymer which in turn equilibrates with the enzyme that oxidizes substrate. The point is that each of the three components serves an individual function which gives an aggregate function not achievable with any one component alone. Gray and co-workers[18] are poised to exploit modified biological redox reagents as semisynthetic enzymes. The specific ideas developed above should serve to illustrate what is meant by multicomponent catalysts and that such catalyst *systems* can, in fact, be made by rational means using existing knowledge.

Photodiode Systems: A Molecular Approach

Scheme II illustrates the familiar "Z-scheme" representing the essential features of the natural system for the conversion of optical energy to chemical energy in the form of redox products derived from CO_2 and H_2O, Eq. (3).[19]



SCHEME II Representation of the "*Z*-scheme" for photosynthesis showing two photosystems and an aggregate system to drive oxidation of H_2O and reduction of CO_2 (Ref. 19).

$$CO_2 + H_2O \xrightarrow{h\nu} O_2 + (CH_2O) \tag{3}$$

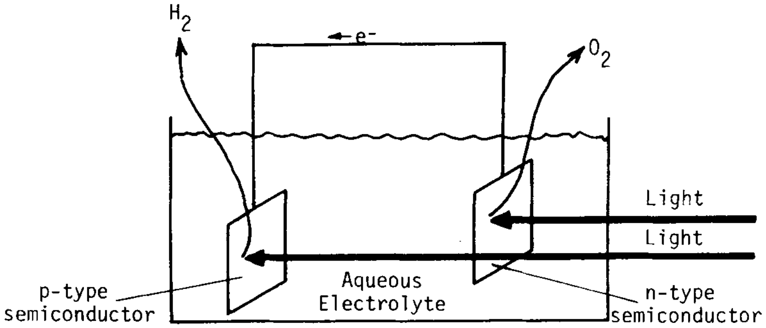
The natural system is clearly one based on molecules, and thus provides an existence proof for molecule-based systems for solar energy conversion. In the area of research aimed at chemical approaches to solar energy conversion and storage there are many examples of efforts to devise chemical systems that mimic the function of the natural photosynthetic apparatus.

There are four important features of the photosynthetic apparatus. First, there is a component for light absorption based on chlorophyll. Second, there is a structured arrangement of electron donor and acceptor reagents that function in such a way that excited state, one-electron reaction of the chlorophyll is irreversible. Electrons are transferred unidirectionally across significant distances to yield geometrically segregated oxidants and reductants. Third, there are catalysts that can apparently equilibrate with one-electron oxidants and reductants to effect the multielectron oxidation of H_2O and reduction of CO_2. Fourth, the system involves *two* photosystems, presumably nature's way of effecting the formation of high energy redox products with good efficiency. It is well known that threshold response solar conversion systems can operate with higher efficiency when more than one light absorption system is used.[20]

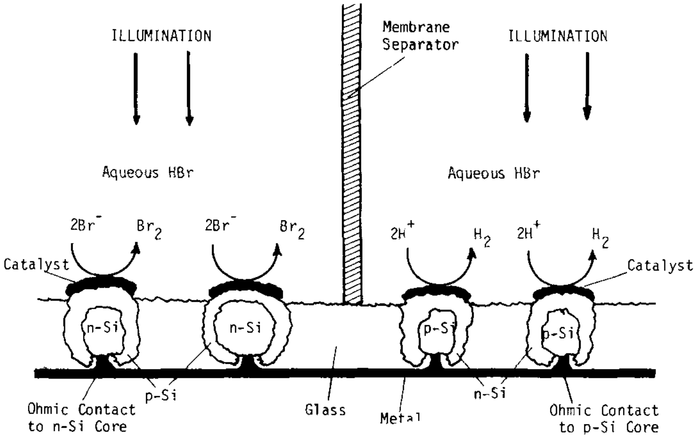
The function of the photosynthetic system can be achieved with semiconductor-based photoelectrochemical cells. Scheme III illustrates a double photoelectrode cell for water splitting.[21] However, such a system is not what would ordinarily be regarded as molecule based, since the solid semiconductor is the light absorber, provides a mechanism for achieving charge separation, and its surface is the "catalyst" for converting one-redox-equivalent-at-a-time photogeneration events to multiequivalent products such as O_2 from H_2O oxidation. Arguably, solid state photovoltaic cells can be used to duplicate the function of photosynthesis by placing the solar cell in series with an electrolyte solution. An especially clever device involves using microspheres of p-n Si, Scheme IV, to effect the process represented by Eq. (4).[22]

$$2HBr \xrightarrow{h\nu} H_2 + Br_2 \tag{4}$$

This device with its various components comes closer to the spirit of what is meant by a chemical system—several components to achieve an aggregate function. In this case, catalysts, structured arrays of microspheres, and the exploitation of a spherical p-n junction



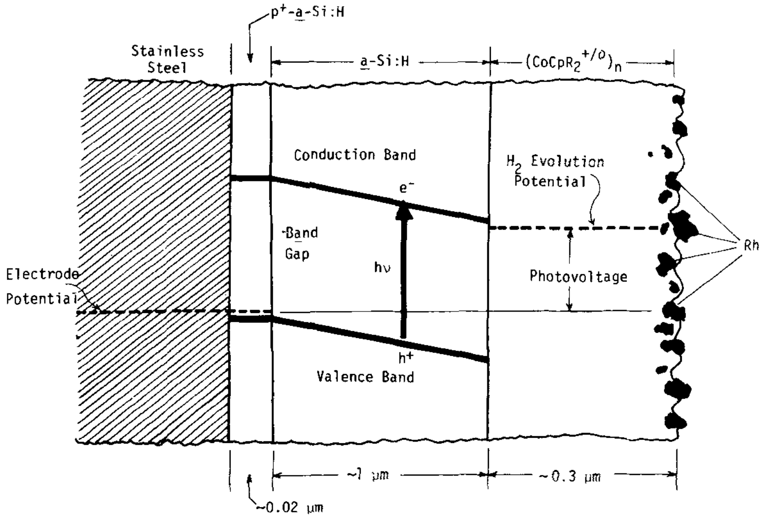
SCHEME III A double photoelectrode-based cell for converting light to chemical energy via the light-driven decomposition of H_2O to H_2 and $1/2O_2$. (Ref. 21). The net reaction requires eight photons per molecule of O_2, four at each photoelectrode, as in the natural photosynthetic system.



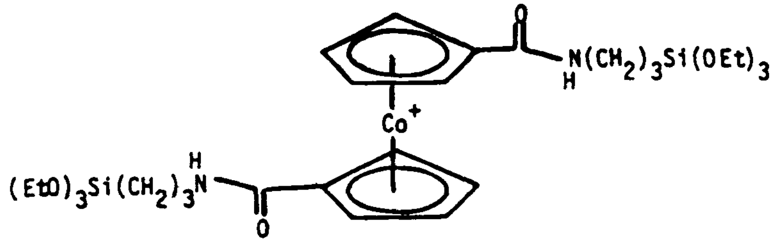
SCHEME IV Texas Instruments system (Ref. 22) for converting sunlight to stored chemical energy via the light-driven decomposition of 2HBr to H_2 and Br_2. Microspheres (~100 μm) of crystalline Si are initially doped to have either a p-core and an n-skin or n-core and p-skin. The microspheres are dispersed into a "monograin" film (in a glass support), etched so that the core can be ohmically contacted, and coated with catalysts for H_2 and Br_2 generation. The result is a system for cleverly having two p-n Si solar cells in series and utilizing Si in an especially effective way.

allow a novel way to effectively put two p-n Si solar cells in series with an electrolyte solution to split HBr with light. However, molecular chemists likely see few avenues for creative contribution in the "synthesis" of such systems.

Semiconductor-based devices for unidirectional electron transfer do, however, afford considerable opportunity for molecular scientists, and inorganic chemists especially. For example, it is now known that catalysis of H_2 evolution from p-type semiconductor photoelectrodes is generally required in order to achieve high efficiency for light-driven reduction of H_2O.[23] The best known catalysts are noble metals,[24] high work function materials that would typically be expected to form an ohmic contact to p-type semiconductors.[20] The formation of an ohmic contact is undesirable, because the photovoltage would be diminished significantly. Assemblies like that represented by Scheme V involve the use of a molecule-based redox polymer such as that derived from hydrolysis of **I** or **III** that provides for a uniform, non-ohmic contact to the p-type semiconductor.[25] The



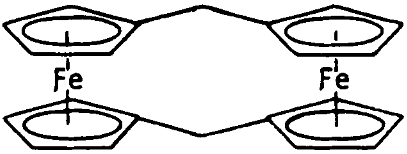
SCHEME V A thin film, catalytic photoelectrode for H_2 evolution (Ref. 25). The *a*-Si : H, intrinsic and p^+-doped, can be made by a deposition from SiH_4, and provides the mechanism for charge separation after photoexcitation. The $(CoCpR_2^{+/0})_nRh$ is a catalyst system for rapidly accepting one-electron-at-a-time from the photoexcited i-*a*-Si : H and effecting H_2 evolution via reduction of H_2O.



III

redox polymers from **I** or **III** have redox potentials that are sufficiently negative that a good photovoltage is expected for many visible light-responsive photocathodes including p-type Si, WS_2, InP, and *a*-Si : H.[25] Catalysis of the H_2 evolution reaction can be effected via equilibration of the Rh particles with the polymer; the Rh serves to equilibrate the redox polymer with the (H_2O/H_2) redox couple. The redox polymer/Rh system is used to convert one-electron-at-a-time photoexcitation events to efficient two-electron reduction of H_2O. The entire assembly mimics one of the photosystems in photosynthesis.

The particulate Rh catalyst for the H_2 evolution, in principle, could be replaced with a molecular catalyst. However, good catalyst molecules, other than the enzyme hydrogenase, for this purpose are not known. Species derived from **IV** are H_2 evolution catalysts, but the turnover frequency is low and the system only works in very strong acid.[26] Replacing the Rh with a non-noble metal-containing catalyst would be important in lowering the cost of the catalyst. For the reasons outlined above in the section on multicomponent catalysts the molecule-based redox polymer can represent a good way to interface the electrode with enzyme catalysts including hydrogenase. A p-type semiconductor/redox polymer/hydrogenase system could duplicate the function of one of the photosystems of photosynthesis with two of the components being molecule based, the electron relay system and the catalyst.



IV

What are the prospects for molecule-based systems to achieve the function of unidirectional, light-driven (up-hill), electron transfer? Absorbing visible light with molecules that can transfer electrons to make high energy redox products is well known[27]; the excited state process represented by Eq. (5)

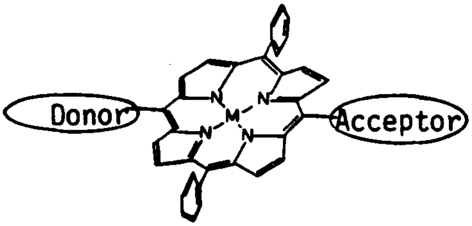
$$[\mathrm{Ru}(2,2'\text{-bipyridine})_3{}^{2+}]^* + \mathrm{MV}^{2+} \xrightarrow{k_5} \mathrm{Ru}(2,2'\text{-bipyridine})_3{}^{3+} + \mathrm{MV}^{+} \quad (5)$$

is but one example.[28] However, exploiting such high efficiency primary product formation is not possible, owing to rapid back electron transfer, Eq. (6),

$$\mathrm{Ru(2,2'\text{-}bipyridine)_3^{3+} + MV^{+}} \xrightarrow{k_5} \mathrm{Ru(2,2'\text{-}bipyridine)_3^{2+} + MV^{2+}} \qquad (6)$$

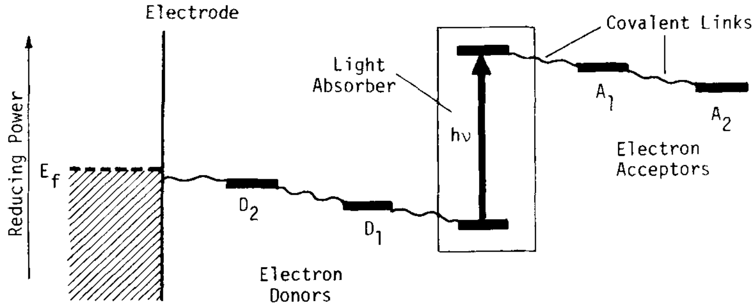
that degrades the excited state energy to heat. It should be possible to assemble macromolecular (nonpolymeric) molecules, built from smaller molecules, that have the function of absorbing light and transferring electrons in only one direction, Scheme VI. At least on paper, a molecule-based system can be devised that will duplicate a crucial part of the photosynthetic apparatus.

A start toward a system as envisioned in Scheme VI has been made by linking an electron acceptor and an electron donor to a porphyrin, V.[29]



V

This follows several reports of linked absorber and acceptor molecules that mimic the primary electron transfer systems in photosynthesis.[30] The three-component molecule macromolecule represented by V re-



SCHEME VI Architecture of a molecular system for light absorption followed by unidirectional electron transfer.

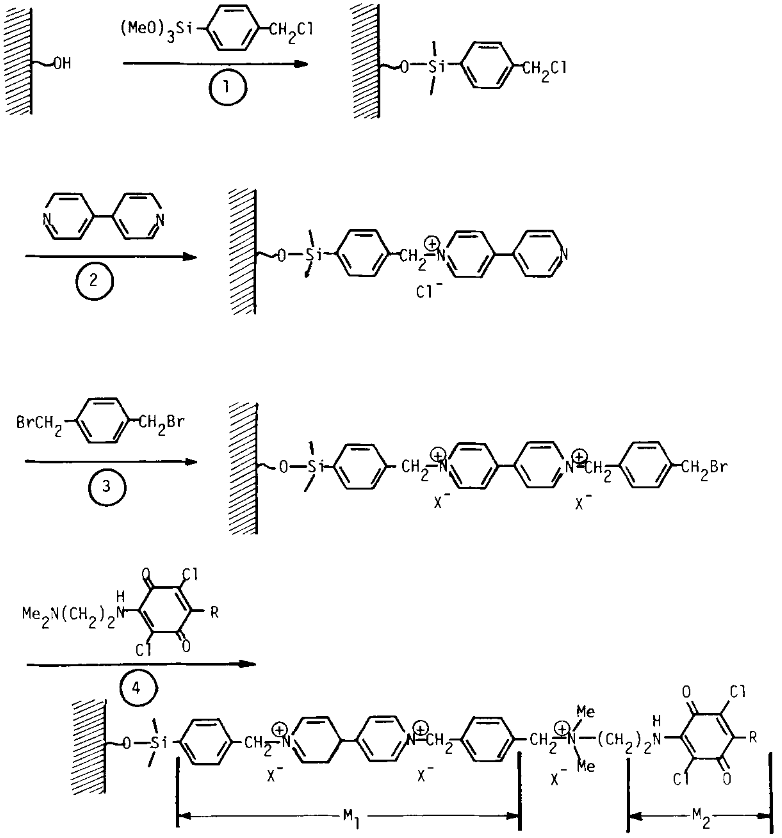
sults in charge separation upon photoexcitation of the visible-light absorbing porphyrin unit as represented in Eq. (7).

$$\boxed{\text{Donor}} \sim \boxed{\text{Absorber}} \sim \boxed{\text{Acceptor}} \xrightarrow{h\nu} \boxed{\text{Donor}^{+}} \sim \boxed{\text{Absorber}} \sim \boxed{\text{Acceptor}^{-}} \tag{7}$$

Such a system illustrates the basic idea, but exploiting such charge separation is still precluded by rapid back electron transfer. What is needed to achieve useful energy conversion is greater geometrical separation between the oxidized donor and the reduced acceptor *and* a method for orienting an assembly of such molecules so that the charges can be collected by electronic conductors to generate electrical energy or by catalysts for irreversible fuel-forming reactions.

Prospects for synthesizing multimolecule-based systems like that represented in Scheme VI seems possible by at least two methodologies, both of which can lead to a useful orientation on an electronic conductor. One synthetic methodology for synthesizing a system for useful light-induced, unidirectional electron transfer involves fabrication of multilayer films using the Langmuir–Blodgett technique.[31] Indeed, elegant work already demonstrates (1) fabrication of well-structured multilayers of significant (~500 Å) dimension; (2) multilayers containing visible-light absorbing capable of long-distance (~20 Å) excited state electron transfer to built-in acceptor molecules in a separate layer; and (3) that multilayers can be deposited on conductors and subsequently metallized to make a front and back contact.[32] In recent years some exciting possibilities have been raised concerning new applications of Langmuir–Blodgett techniques involving novel examples of monolayer film-forming molecules.[32,33]

A second synthetic methodology for systems like that in Scheme VI is inspired by the Nobel Prize winning work of Merrifield,[34] the "solid phase" synthesis of large macromolecules (nonpolymeric, proteins) based on simple molecule building blocks, amino acids. The key to this synthetic methodology for the function of optical energy conversion is to use building blocks having functionality so that coupling can be carried out in a manner that yields an ordered arrangement of a light absorber and various electron donors and acceptors. Such solid phase synthesis can begin on electronic conductors to achieve the ultimate aim of efficient charge collection. The thrust of the idea is illustrated by the four-step process in Scheme VII that has recently been demonstrated[35] as a prelude to an effort to synthesize a complete system like that illustrated in Scheme VI. After the first step each successive step is the alkylation of a nitrogen. As in the Merrifield resin synthesis of a protein, the isolation of product occurs after each step by a physical separation of the solid. The result of the chemistry is a SnO_2-bound macromolecule consisting



SCHEME VII Solid phase synthesis of a surface-confined macromolecule consisting of two redox units, M_1 = a derivative of N,N'-dibenzyl-4,4'-bipyridinium and M_2 = a derivative of 2,5-dichloro-*p*-benzoquinone (Ref. 35).

of two redox subunits, a viologen derivative and a quinone. Note that the quinone bears a pendant $-NMe_2$ group that can be alkylated in subsequent steps. It is apparent that a resin synthesis of macromolecules, consisting of well-defined redox subunits, in an ordered array, and bound to a conductor, can be fruitful.

Molecule-based systems for light-induced charge separation do not function by the same mechanism as in semiconductor-based devices, but nonetheless the same net result can be achieved. In solid state devices photogenerated carriers are separated by the strong electric field associated with a p-n junction, semiconductor/metal interface, semiconductor/liquid electrolyte interface, or a photoconductor sandwiched between two conductors of different work function. The molecule-based systems achieve the function of useful charge separation via a series of thermodynamically down-hill redox events carrying reducing equivalents to a site geometrically distant from the site of oxidation in an ordered array of redox units. There are at least two concrete pathways by which such molecule-based systems can be synthesized, each with some precedent and each with advantages and disadvantages.

CHEMICAL SYSTEMS INSPIRED BY MICROELECTRONICS

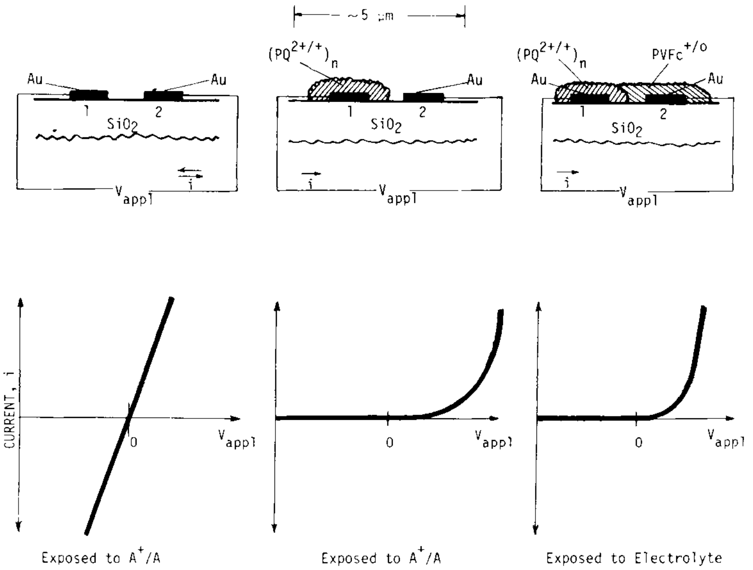
By themselves the chemical components of microelectronic devices do not suggest that remarkable functions can be achieved. But clever organization of pedestrian semiconductors (Si, GaAs), metals (Au, Al), insulators (SiO_2, Si_3N_4) and dopants (B, P) makes possible the recent revolution in electrical engineering and computer science. Coupled with microfabrication techniques, the aggregate function that can be achieved from properties of electronic materials allows discrete devices such as diodes, transistors, lasers, and capacitors to be prepared in high density essentially in a two-dimensional world, largely founded in elemental Si, except for optical devices. An appropriately organized array of discrete devices comprises an integrated circuit that allows larger functions to be realized than is possible with a discrete device which itself is typically prepared from several materials. It would appear possible to assemble chemical systems that achieve some of the functions of discrete solid state devices. Even "integration" of such systems appears plausible. The small crucial dimensions of state-of-the-science microelectronics (submicron) can be spanned by macromolecules or organized molecular assemblies such as Langmuir–Blodgett multilayers. Thus, there is an opportunity to interface chemical (and biological) systems with solid state components prepared using more or less conventional microfabrication techniques. Employing microfabricated solid state components in synthetic, molecule-based chemical systems is analogous to using a natural enzyme as a component in a synthetic, molecule-based system inspired by natural systems. Two discrete microelectronic devices can be used to illustrate some of the issues here: diodes and transistors. Chemical systems, based on molelcules as the crucial elements, can be fabricated which duplicate some of the properties of these devices. Molecule-based devices inspired by solid state microelectronics are not destined to replace solid state devices on a near term timescale; rather the new devices may be useful for new applications where solid state devices may not be as useful. An especially promising practical application would be microsensors.

Devices Inspired by Diodes

Diodes are devices that allow current to pass upon the application of a potential in one direction but not when the applied potential is equal in magnitude but opposite in direction. Electrochemical devices, in general, can be configured in such a way that diode-like current–voltage curves can be obtained. However, recent work[36] on purposefully modified electrodes demonstrates clearly the ability to rationally prepare molecule-based diodes with crucial dimension (contact-to-contact) of less than 1 μm. In solid state systems diode behavior can be obtained when two different materials are placed in electrical contact with one another, e.g., metal/semiconductor or p-/n-type semiconductor. Likewise, in electrochemical diodes, diode behavior can be brought about by placing two different (molecule-based) materials in contact with one another. The analogy can be extended further by noting that the diode behavior of the ideal solid state devices depends in large measure on the difference in the work functions of the two materials. For electrochemical devices the diode current–voltage curves depend on the difference in the formal electrochemical potential of the two materials—the equivalent of the differences in the work function of the two solid state materials of a conventional diode. Thus, molecule-based diodes are devices having properties that can be controlled by variation in the properties of the molecules that comprise them.

Scheme VIII illustrates several types of electrochemical devices presented within the framework of illustrating that rational synthesis of molecule-based diodes is possible. Consider first the situation represented by a cell having two equal area electrodes that are reversible to the redox couple A^+/A present in the solution such that $[A] = [A^+]$. Assuming that there are no electroactive materials other than A^+ and A, application of a potential in either direction results in current flow such that A is oxidized to A^+ at one electrode and A^+ is reduced to A at the other, a symmetrical current–voltage curve about zero applied potential results.

To make the example in Scheme VIII more explicit, consider the redox couple to be $Fe(\eta^5\text{-}C_5H_5)_2^{+/0}$, $E^{0'} \approx +0.45$ V vs. SCE,[37] in



Exposed to A+/A

Exposed to A+/A

Exposed to Electrolyte

SCHEME VIII Two terminal microelectrochemical devices. (a) Both electrodes reversible to A^+/A; (b) one redox polymer modified electrode only capable of reducing A^+ to A; and (c) two redox polymer modified electrodes with a polymer/polymer contact such that current flows upon application of a potential sufficient to oxidize one polymer and reduce the other. In the current–voltage curves the voltage to the right of zero is for the positive lead connected to electrode 2 (Ref. 39).

$CH_3CN/0.1$ *M* $[n\text{-}Bu_4N]ClO_4$. If one of the electrodes is modified with polymer derived from **I** then that electrode is no longer reversible to the $Fe(\eta^5\text{-}C_5H_5)_2^{+/0}$ redox couple.[38] Rather, only the reduction of $Fe(\eta^5\text{-}C_5H_5)_2^+$ to $Fe(\eta^5\text{-}C_5H_5)_2^0$ can be effected, Eq. (8).

$$(PQ^+)_n + n\,Fe(\eta^5-C_5H_5)_2{}^+ \xrightarrow{k_8} (PQ^{2+})_n + n\,Fe(\eta^5-C_5H_5)_2{}^0 \tag{8}$$

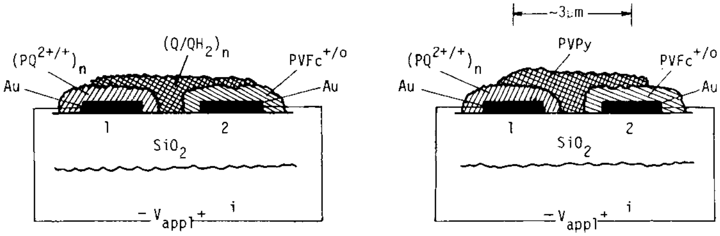
Moreover, the reduction can only be effected when the potential of the $(PQ^{2+/+})_n$-modified electrode approaches the formal potential of the $(PQ^{2+/+})_n$ redox system, ~ -0.55 V vs. SCE. Thus when a potential is applied to the two electrodes, significant current passes only when the negative lead is attached to the $(PQ^{2+/+})_n$-modified electrode. Moreover, the potential required is of the order of $\sim$0.9 V, the difference in $E^{0\prime}$'s of the $(PQ^{2+/+})_n$ and the $Fe(\eta^5\text{-}C_5H_5)_2^{+/0}$. Significant current does not flow when the potential is applied in the opposite direction, because the reverse of the reaction represented by Eq. (8) is up-hill by $\sim$0.9 V. $Fe(\eta^5\text{-}C_5H_5)_2^0$ can penetrate the $(PQ^{2+})_n$ polymer and be oxidized at the electrode surface. The current from such penetration will represent a contribution to the leakage current, but to the extent that penetration can be prevented the cell has a diode-like current–voltage curve with a threshold voltage more or less given by the difference in $E^{0\prime}$'s of the two molecule-based components.

The final portion of Scheme VIII illustrates a microelectrochemical diode based on the principles developed in the preceding paragraph.[39] In this case both of the molecule-based materials are immoblized onto closely spaced microelectrodes such that the two redox polymers "contact" each other. The $(PQ^{2+/+})_n$ system is again derived from **I** and the $PVFc^{+/0}$ is the polyvinylferrocene redox system. As in the case where the $Fe(\eta^5\text{-}C_5H_5)_2^{+/0}$ system is in solution, current flow occurs upon application of potential in one direction; at the $(PQ^{2+/+})_n/PVFc^{+/0}$ interface charge only passes in one direction, analogous to the redox reaction given by Eq. (8). Moreover, since both molecule-based systems are immoblized the only mechanism for charge transport from one microelectrode to the other is via electron transfer through the polymer connecting one electrode with another.

The structural arrangement of the system is such that the molecule-based materials contact each other but each is in turn only in contact with one microelectrode. The only mechanism for charge transport from one microelectrode to the other is via a path that is unidirectional owing to the large driving force for the process represented by Eq. (8). Unlike the system where only one of the components is immoblized, there is no leakage current attributable to penetration of one molecule-based material into another. The small spacing between the microelectrodes allows significant steady state current to pass, despite the low "conductivity" of the redox polymers.

As developed above, the synthesis of a diode by interfacing two different molecule-based materials with closely spaced microelectrodes has been effected by a rational strategy.[39] The asymmetrical current–voltage characteristic can be achieved. However, useful solid state diodes operate at high frequencies; the microelectrochemical diodes are not likely to be competitive in this respect. The time required to switch the microelectrochemical diode is that needed to effect a change in redox state of a molecule-based material. Oxidation and reduction of electrode-confined polymers can be effected on timescales of the order of 10^{-3} s for thicknesses of ~0.5 μm in the best cases. Diodes derived from molecule-based materials may have other properties that make them useful. Sensor applications are most easily envisioned in that the diode characteristics can be influenced by the chemical properties of the environment in a rational way.

As an example of a diode whose properties will depend on the chemical environment in a rational way consider the system repre-



SCHEME IX (a) A microelectrochemical diode with a current that can be modulated by the solution pH, since the $E^{0'}$ of the $(Q/QH_2)_n$ is pH sensitive and the $E^{0'}$'s of the $(PQ^{2+/+})_n$ and $PVFc^{+/0}$ polymers are independent of pH, and (b) a diode that responds to two chemical stimuli, pH and the presence of $Fe(CN)_6^{3-/4-}$ (Ref. 40).

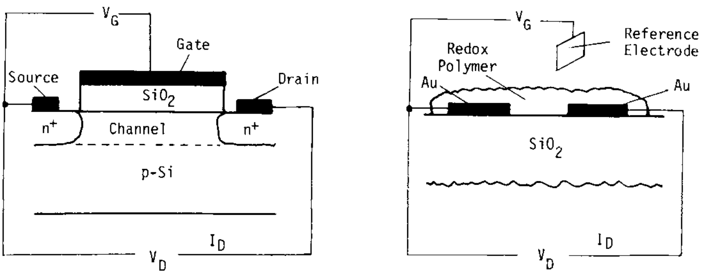
in a way that places a third molecule-based material, $(Q/QH_2)_n$, between the $(PQ^{2+/+})_n$ and $PVFc^{+/0}$ such that the only mechanism for charge transport from one microelectrode to the other is via the three molecule-based materials.[40] The key is that the formal potential of the $(Q/QH_2)_n$ layer is pH-dependent, whereas the $E^{0\prime}$'s of the other two molecule-based materials are pH-independent. Only when $E^{0\prime}(Q/QH_2)_n$ is between $E^{0\prime}(PQ^{2+/+})_n$ and $E^{0\prime}(PVFc^{+/0})$ will electrons pass from the $(PQ^{2+/+})_n$-coated microelectrode. The *pH of the environment* will control the $E^{0\prime}$ of the $(Q/QH_2)_n$ layer and variations in pH should, therefore, lead to variations in the current that can pass at an applied potential of ~0.9 V when the negative lead is attached to the $(PQ^{2+/+})_n$-coated microelectrode. Variations in this theme, Scheme IX, can lead to a diode where the steady state current depends on the simultaneous presence of two chemical stimuli.[40] For example, consider replacing the $(Q/QH_2)_n$ layer with polyvinylpyridine, PVPy. In an aqueous electrolyte the pyridine nitrogens can be protonated to form $PVPyH^+$.[41,42] However, the $PVPy/PVPyH^+$ system does not have an $E^{0\prime}$ between $E^{0\prime}(PQ^{2+/+})_n$ and $E^{0\prime}(PVFc^{+/0})$. Thus, protonation alone does not turn on current. The $PVPyH^+$, though, can electrostatically bind *very low* concentrations of $Fe(CN)_6^{3-/4-}$,[41] a redox couple with a formal potential between $E^{0\prime}(PQ^{2+/+})_n$ and $E^{0\prime}(PVFc^{+/0})$. What is achieved with the PVPy component is a system that passes current when both $[H^+]$ and $[Fe(CN)_6^{3-/4-}]$ are above certain values. Neither H^+ nor $Fe(CN)_6^{3-/4-}$ alone will allow current to pass.

The ideas and systems developed in the foregoing discussion stem from research on the modifications of macroscopic electrodes.[36] Work by Murray,[43] especially, has established many of the basic concepts that can now be exploited, together with microfabrication, to synthesize new microelectronic devices. Indeed, Murray first demonstrated molecule-based diodes by functionalizing macroscopic electrodes with a "bilayer" of two different molecule-based polymers followed by depostion of a porous front contact to yield a "sandwich" structure with the crucial dimension being the thickness of the sandwich.[43] The systems represented in Schemes VIII and IX can be regarded as miniature, open-faced sandwiches. There are many synthetic methodologies to be applied in devising molecule-based diodes and many challenges for molecular chemists. The utility of the diode systems will depend on the molecular properties of the components; durability, charge transport rates, and sensor specificity are key areas.

Devices Inspired by Transistors

Narrowly defined, a transistor is a device that changes its resistance in response to an electrical signal.[20] This function is technologically very significant and existing applications for conventional transistors will be met by solid state devices. Nonetheless, a discrete Si/SiO_2/metal field effect transistor, a so-called MOSFET (metal oxide semiconductor field effect transistor), bears many analogies to molecule-based transistors fabricated recently.[44] For molecule-based devices the nearest term application envisioned is to amplify chemical signals rather than to amplify electrical signals—a typical function of solid state transistors.

To develop the analogy between molecule-based transistors and MOSFET devices[20] consider Scheme X. By changing the gate potential, V_G, of the MOSFET the region in the Si between source and drain and just beneath the SiO_2, the "channel," can be changed from p-type Si (as in the bulk) to a region heavily n-type, or inverted in carrier density compared to the bulk; the Fermi level for electrons, E_f, can be moved from near the top of the valence band of the Si at the Si/SiO_2 interface to the bottom of the conduction band of the Si at the Si/SiO_2 interface. The consequence of carrier inversion in the channel is that at a fixed potential difference between source and drain, V_D, current flows between source and drain; the channel is said to be "open" and the device "on." When E_f is such that the channel region is p-type—like the bulk, $I_D = 0$ because the current path between source and drain is blocked by the nature of the n^+-p-n^+ junctions. For the purpose here the crucial point is that a variation of V_G of less than 1 V results in a small amount of charge



SCHEME X (a) A conventional Si MOSFET (Ref. 20) and (b) a molecule-based transistor (Refs. 44–47).

sented by Scheme IX where the diode in Scheme VIII is elaborated transfer, gate current, I_G, that dramatically changes the rate of charge transfer from source to drain at a given value of V_D. A MOSFET is typically turned off and on at $> 10^6$ Hz; the source–drain distance, channel length, is ~1 μm in state-of-the-technology memory arrays; the ΔV_G is ~0.5 V; and the charge needed to open a closed channel can be as small as 10^{12} charges/cm^2 of gate area.

A molecule-based microelectronic device that functions as a transistor can be synthesized by coating two closely spaced microelectrodes, source and drain, with a polymer, the channel material, that has the property that a change in conductivity can be brought about by changing the electrochemical potential, Scheme X.[44–47] A polymer such as polyaniline has been demonstrated to be effective[46]: I_D has been shown to vary by ~10^7 upon a change in V_G of 0.5 V at $V_D = 0.2$ V. While the similarities between the MOSFET and the molecule-based device are readily apparent there are three significant differences as well. First, the I_G in the molecule-based device is faradaic—chemical oxidation and reduction occur to open and close the channel, whereas in the MOSFET the I_G is capacitive. The faradaic current necessarily involves movement of ions, a slower process than the movement of electrons in the solid state device. Accordingly, the molecule-based device will operate at much lower frequencies. Second, the molecule-based devices fabricated so far involve the use of a relatively large volume channel compared to the channel of a MOSFET, because the polymer is thick. Thus, though the source–drain separation is the same, the molecule-based device requires more charge to open and close the channel. Therefore, despite a similar ΔV_G to open and close the channel the molecule-based device will consume more power, and this, coupled with the low mobility of ions, results in a molecule-based device that will only give power amplification at low frequencies. Improvements in the molecule-based devices will be made, but near-term competition for solid state transistors in conventional applications is *not* realistic for any chemical or biological alternative.

The third difference between a solid state transistor and the molecule-based transistor may provide opportunities for practical applications: the channel of the molecule-based device can respond directly to chemical signals; in general, the channel properties will depend on the medium in which it is immersed (solvent, electrolyte, etc.); and the V_G dependence of I_D at fixed V_D can be quite different for the molecule-based device than for the MOSFET and depends on the channel material—a useful variable in the molecule-based device. Applications as sensors appear to follow from the properties of molecule-based transistors, especially when the device is elaborated with other molecular components to build in specificity to particular chemical signals.

Molecule-based transistor devices based on poly-3-methylthiophene illustrate one potential advantage of such a sensor.[47] The dependence of I_D and V_G reveals a characteristic that is at least as good as a state-of-the-art MOSFET; a change in the redox potential, ΔE redox, of the solution in contact with the channel can cause a change in I_D, ΔI_D, that may be larger than can be obtained from a similiar ΔV_G in solid state devices. However, whether a given redox reagent will equilibrate with the channel depends on the kinetics. Catalysts deposited onto, or dispersed throughout, the channel can endow the surface with a mechanism for equilibration with reagents that have slow kinetics such as O_2 or H_2.[46] Attachments of enzymes directly onto the channel materials will allow specific reagents to be detected. Organized arrays of molecule-based transistors can be used to obtain a "fingerprint" response to a chemical environment. The point is that the remarkably strong dependence of I_D on V_G of certain molecule-based channel materials, coupled with the use of other molecular components, such as enzymes or synthetic redox catalysts, will allow the development of chemical detectors.

Another interesting fact is that the qualitative shape of the I_D vs. V_G curve can be different for the molecule-based device compared to the MOSFET. A particular example is the polyaniline-based device[46] that shows a *maximum* in I_D at a particular value of V_G and ± 0.2 V around this value I_D falls by severals orders of magnitude. This means that if a redox reagent is used to open the channel then only certain redox reagents will be thermodynamically well matched to the purpose. By using a thin layer of a conventional redox polymer, e.g., $PVFc^{+/0}$, on one microelectrode sandwiched between the channel material it may be possible to manipulate further the redox region where the device is turned on, since such an arrangement of two redox polymers can function as a diode as described in the preceding section. But when the $PVFc^{+/0}$ is very thin the maximum magnitude of I_D will be largely controlled by the channel material spanning most of the region between the source and drain. The assertion is that molecule-based transistors, particularly ones based on two or more components, can be specific chemical detectors with a recognition step leading directly to amplification with the same system.

A FUTURE FOR SYNTHESIS OF CHEMICAL SYSTEMS

The four specific examples of "synthetic targets," multicomponent catalysts, optical energy conversion systems, diodes and transistors, represent modest but nonetheless complicated extensions of what is known. Doubtless there will be those who hold the view that such chemical synthesis is too applied to represent a pure research endeavor and that the preparation of so-called chemical system is a mere, but expensive, summation of existing knowledge. However, taken to the extreme, such a view should lead to the demise of chemistry as an experimental science. After all, thermodynamics and quantum mechanics should be able to provide the predictive power needed for molecular or systems synthesis. It is the view of this author that systems synthesis is an important step in the development of new applications of molecular science, but there are a multitude of basic knowledge areas that will require major expansion prior to achieving significant practical impact. These include reactions at interfaces, physical characterization techniques, synthetic and purification methods for macromolecular assemblies, and theoretical understanding of aggregate systems. Systems synthesis will require greater resource expenditure; there will be a new level of interdisciplinary effort required *within* and between groups; the research work will have longer gestation periods before the fruits will reach maturity; greater levels of patience are required from investigators and funding agencies; more planning for longer term projects will be required. The power of molecular synthesis is great—it is time to add a new dimension to synthesis that is already, and will continue to be, rich in practical value. Catalysts, dyes, drugs, insecticides, and other single-component, molecular materials will continue to be important, but there is much fundamental and, potentially, practical pay-off in the synthesis of multicomponent, molecule-based systems. Rather than the traditional macroscopic to microscopic in electronics, there is a genuine opportunity for the fabrication of new systems from the "molecule up." Such devices may lead to new technological opportunities inspired by the existence of molecule-based biological systems for memory, pattern recognition, vision, and energy conversion.

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References

1. R. B. Woodward, Pure Appl. Chem. **33**, 145 (1973).
2. A. Werner, Z. Anorg. Chem. **3**, 267 (1893).
3. Cf., for example, the numerous contributions cited in *Organic Synthesis via Metal Carbonyls,* Vol. 1, I. Wender and P. Pino, eds. (Interscience, New York, 1968).
4. E. O. Fischer and W. Pfab, Z. Naturforsch. B **7**, 377 (1952).
5. G. Wilkinson, M. Rosenblum and M. C. Whiting, J. Am. Chem. Soc. **74**, 2125 (1952).
6. J. A. Bertrand, F. A. Cotton and W. A. Dollase, J. Am. Chem. Soc. **85**, 1349 (1963) and Inorg. Chem. **2**, 1166 (1963).
7. J. M. Berg and R. H. Holm, Met. Ions Biol. **4**, 1 (1982).
8. T. Katsuki and K. B. Sharpless, J. Am. Chem. Soc. **102**, 5974 (1980).
9. B. Bosnitich and N. K. Roberts, Adv. Chem. Ser. **196**, 337 (1982).
10. J. Sancho and R. R. Schrock, J. Mol. Catal. **15**, 75 (1982).
11. R. R. Durand, Jr., C. S. Bencosne, J. P. Collman and F. C. Anson, J. Am. Chem. Soc. **105**, 2711 (1983).
12. (a) D. C. Bookbinder, N. S. Lewis and M. S. Wrighton, J. Am. Chem. Soc. **103**, 7656 (1981); (b) S. Chao, R. A. Simon, T. Mallouk and M. S. Wrighton (to be submitted).
13. M. M. Rosen and A. I. Krasna, Photochem. Photobiol. **31**, 259 (1980).
14. L. A. Summers in *The Bipyridinium Herbicides* (Academic, London, 1980), pp. 122–124.
15. A. M. Klibanov, Science **219**, 722 (1983).
16. S. Chao, J. L. Robbins and M. S. Wrighton, J. Am. Chem. Soc. **105**, 181 (1983).
17. D. M. Novak, B. V. Tilak and B. E. Conway in *Modern Aspects of Electrochemistry, No. 14,* J. O'M. Bockris, B. E. Conway, and R. E. White, eds. (Plenum, New York, 1982).
18. D. C. Nocera, J. R. Winkler, K. M. Yocum, E. Bordignon and H. B. Gray, J. Am. Chem. Soc. **106**, 5145 (1984).
19. J. Livorness and T. D. Smith, Struct. Bond. **48**, 1 (1982).
20. S. M. Sze, *Physics of Semiconductor Devices,* 2nd ed. (Wiley, New York, 1981).
21. M. S. Wrighton, Acc. Chem. Res. **12**, 303 (1979).
22. (a) J. S. Kilby, J. W. Lathrop and W. A. Porter, U.S. Patents 4,021,323, May

3, 1977; 4,100,051, July 11, 1978; and 4,136,436, January 30, 1979; (b) E. L. Johnson in *Electrochemistry in Industry*, U. Landau, E. Yeager and D. Kortan, eds. (Plenum, New York, 1982), pp. 299–306.
23. A. Heller, Science **223**, 1141 (1984).
24. J. O'M. Bockris and A. K. N. Reddy, *Modern Electrochemistry*, Vol 2 (Plenum, New York, 1970), p. 1238.
25. (a) D. J. Harrison, G. S. Calabrese, A. J. Ricco, J. A. Dresner and M. S. Wrighton, J. Am. Chem. Soc. **105**, 4212 (1983); (b) R. N. Dominey, N. S. Lewis, J. A. Bruce, D. C. Bookbinder and M. S. Wrighton, J. Am. Chem. Soc. **104**, 467 (1982); (c) K. A. Daube, D. J. Harrison, T. E. Mallouk, A. J. Ricco, W. A. Hendrickson, A. J. Drube, S. Chao and M. S. Wrighton, J. Photochem. (in press); (d) J. A. Baglio, G. S. Calabrese, D. J. Harrison, E. Kamieniecki, A. J. Ricco, M. S. Wrighton and G. D. Zoski, J. Am. Chem. Soc. **105**, 2246 (1983).
26. U. T. Mueller-Westerhoff and A. Nazzal, J. Am. Chem. Soc. **106**, 5381 (1984).
27. N. Sutin and C. Creutz, J. Chem. Ed. **60**, 809 (1983).
28. C. R. Bock, T. J. Meyer and D. G. Whitten, J. Am. Chem. Soc. **96**, 4710 (1974).
29. M. R. Wasielewski, M. P. Niemczyk, P. Gast and J. R. Norris, presented at the Eighth DOE Solar Photochemistry Research Conference, June 11–14, 1984. (The Proceedings are available from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, Virginia 22161.)
30. M. R. Wasielewski and M. P. Niemczk, J. Am. Chem. Soc. **106**, 5043 (1984) and references cited therein.
31. K. B. Blodgett and I. Langmuir, Phys. Rev. **51**, 964 (1937).
32. (a) H. Kuhn, Pure Appl. Chem. **51**, 341 (1979) and **53**, 2105 (1981); (b) D. Mobius Acc. Chem. Res. **14**, 63 (1981).
33. Cf. Thin Solid Films, **99**, (1982) (Proceedings of the International Conference on Langmuir–Blodgett Films, Durham, England, Sept. 1982).
34. R. B. Merrifield, J. Am. Chem. Soc. **85**, 2149 (1963).
35. D. K. Smith and M. S. Wrighton (unpublished results).
36. R. W. Murray in *Electroanalytical Chemistry*, Vol. 13, A. J. Bard, ed. (Marcel Dekker, New York, 1984), p. 191.
37. N. S. Lewis and M. S. Wrighton, ACS Symposium Series **146**, 37, (1981).
38. N. S. Lewis and M. S. Wrighton, J. Phys. Chem. **88**, 2009 (1984).
39. G. P. Kittlesen, H. S. White and M. S. Wrighton (submitted for publication).
40. Work directed toward the fabrication of the systems represented by Scheme IX is underway in the Wrighton laboratories.
41. N. Oyama and F. C. Anson, J. Electrochem. Soc. **127**, 247 and 640 (1980); Anal. Chem. **52**, 1192 (1980).
42. G. J. Samuels and T. J. Meyer, J. Am. Chem. Soc. **103**, 307 (1981).
43. P. G. Pickup, W. Kutner, C. R. Leidner and R. W. Murray, J. Am. Chem. Soc. **106**, 1991 (1984) and references cited therein.
44. H. S. White, G. P. Kittlesen and M. S. Wrighton, J. Am. Chem. Soc. **106**, 5375 (1984).
45. G. P. Kittlesen, H. S. White and M. S. Wrighton, J. Am. Chem. Soc. **106**, 7389 (1984).
46. E. W. Paul, A. J. Ricco and M. S. Wrighton, J. Chem. Phys. **89**, 1441 (1985).
47. J. W. Thackeray, H. S. White and M. S. Wrighton (to be submitted).