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Fundamentals in the Design of Molecular Electronic Devices: Long-Range Charge Carrier Transport and Electronic Coupling

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A. Introduction

Virtually all molecular electronic devices rely on the interplay between spatial organization and electronic motion to attain the resolution and responsiveness necessary for practical applications.[1] An efficient optical computer,[2] for example, will need a set of precisely positioned chromophores that can be individually addressed and that can reliably produce detectable electrical signals. The device itself must be relatively large compared with a simple molecule, but tiny on a macroscopic scale, to preserve the possibility of chemical accessibility, structural complexity, and general utility. Such arrays are often referred to as "nanoscopic", and their potential utility in devices is one important reason for worldwide interest in "nanotechnology".[3]

Long-range nanoscopic ordering can be attained with either specifically designed block copolymers or low molecular weight species that can arrange themselves into supramolecular arrays, e.g., liquid crystals, micelles, vesicles, tubules, etc.[4] An efficient optoelectronic device will also incorporate an energy gradient that permits vectorial electron motion and signal amplification,[5] ideally with sufficient time resolution to permit each electronic signal to be differentiated from an alternately placed neighbor. These requirements are not easily met, particularly not simultaneously.

In principle, the required chromophore positioning can be attained by either of two methods: by sequential bond-by-bond synthesis or by taking advantage of spontaneous self-assembly or aggregation into stable two- and three-dimensional structures. The structures of the resulting assemblies can then be inferred from spectroscopic or kinetic measurements. From the known distance dependencies of energy transfer[6] and electron-transfer quenching[7] or from the observed shifts of spectral energies and intensities, the local order and the character of interchromophore interactions are then established.[8] Both assembly techniques have been used in our group, and some examples are presented in this Account to illustrate the comparative advantages and difficulties associated with each.

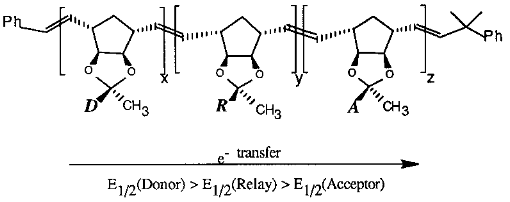
This Account is thus an attempt to describe to readers new to this area the key design features for model compounds relevant to this class of materials. We also illustrate the utility of photoinduced electron transfer in the characterization of these compounds.

We do not yet understand in detail the complexities of either the intramolecular electronic interactions operative in structurally complex molecules or the influence of noncovalent intermolecular interactions on the properties of these same species in three-dimensonally ordered arrays. If we are to ever exploit the practical applications of the optoelectronic materials, however, we must first understand how to control these key intermolecular interactions. In the following sections, therefore, we survey the efforts of our research group in the last several years to define the several factors that must be incorporated into a practical molecular electronic device.

Specifically, we consider (1) how to construct complex nanostructures with precise positioning of the photoresponsive chromophores, (2) how a nanoscale energy cascade can dictate the direction of electron flow, and (3) how electrical fields felt along the migratory pathway of a charge carrier influence its mobility.

B. Spatial Definition of Nanoscale Structures

To obtain macromolecular arrays that might be useful as components in a nanoscaled device, it is necessary to develop dependable synthetic methods that allow reliable construction of high molecular weight molecules in which the position of each of the photoresponsive groups is known precisely. We have employed two quite different approaches to this problem: (1) oligomerization of chromophore-labeled units into rigid, multiple block copolymers **1** and (2) self-assembly of ω-functionalized alkanethiols on freshly deposited metal surfaces **2**.



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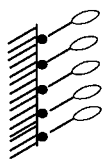

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1. Synthesis of Rigid Block Copolymers Bearing Spectroscopic Probes. If precise positioning of a group of electron or energy relays is to be achieved by the attachment of such groups onto a fixed backbone, the

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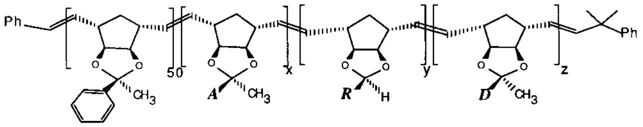
scaffold onto which the addressable groups must be affixed must be conformationally defined. This goal is most easily achieved if the backbone is rigid and if the distances between attached groups can be defined by measurement (e.g., crystallographic characterization of the solid state) or by reliable calculations. Thus, an effective synthetic method will not only provide a pure high polymer of narrow molecular weight range, but also a material which is conformationally rigid, at least on the time scale of the charge transport event.

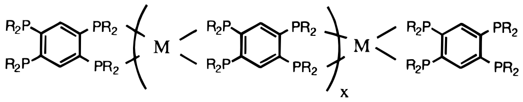
Within the past decade, ring-opening metathesis polymerization (ROMP) has been developed as an effective method for the preparation of highly monodisperse polymers.[9,10] Not only can macromolecules of defined length be attained under mild conditions,[11] but the "living" nature of the key metalloalkylidene intermediate permits the sequential attachment of additional blocks (derived from a structurally altered monomer) whose lengths are precisely controlled by careful choice of the monomer-to-initiator ratio. This method permits the construction of triblock copolymers such as **3**, in which a series of chromophores are confined to individual block sites. With such compounds, we have used fluorescence spectroscopy and laser flash photolysis to show that both energy and electron migration can easily take place, both along one block and across the interface between blocks.[12] The electronic couplings necessary for efficient migration can involve either a singlet or a triplet surface.[13,14]



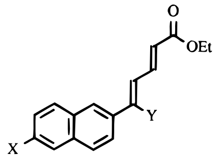
3: **A**=2,5-dicyanophenyl, x=5, **R**=3-phenanthryl, y=10, **D**=3-(N,N-dimethylanilino), z= 5

A key feature necessary for spatial definition of this sort of charge carrier migration is that the polymer backbone be rigid, i.e., that the complications associated with equilibrium interconversion among significantly different conformations be avoided. Both calculational studies and experimental photophysical measurements indicate that this backbone rigidity is attained in the chromophore-labeled polynorbornenes obtained from functionalized norbornenyl precursors. ROMP polymerization to access the family represented by **3** does indeed provide such a structurally rigid backbone.[15] But this backbone is clearly not unique. For example, our group has shown that varying degrees of rigidity can be attained in labeled polyisocyanides produced by organometallic catalytic polymerization of functionalized isocyanide **4**,[16] in group-transfer polymerizations of some vinyl monomers,[17] and in organometallic coordination polymers such as **5**.[18,19] It is also clear that recently developed methods for living radical[20] or cation[21] polymerization would also likely be excellent methods for synthesis of the requisite rigid, monodisperse polymers.

$ArCH_2CH_2NC$
4



5: M = Ni^{II}, Pd^{II}, Pt^{II}



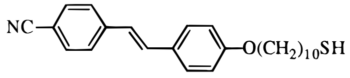
6 a: X, Y = H
b: X=*t*-Bu; Y=H

This is not to say that all useful polymerization methods are directly adaptable to the preparation of rigid materials. Group-transfer polymerization,[22] one of the most useful routes to monodisperse living polymers, often provides conformationally flexible products, even when an additional conjugative group is introduced into the monomeric backbone, as in the polymer derived from **6**.[23]

2. Surface Anchoring as a Route to Spatial Positioning of Photoresponsive Self-Assembled Monolayers. An effective means for positioning an excited state at a defined distance from an electrical contact is to modify a metal or semiconductor surface by formation of a self-assembled monolayer (SAM) in which the terminal position of the adsorbate bears a photoactive group (e.g., **2** in which the open circles represent a photosensitive unit and the filled circles represent surface-compatible binders such as silanes on metal oxides or sulfides on noble metals). Such monolayers are easily produced by simply soaking a freshly deposited metal or metal oxide surface (e.g., gold, silver, copper, mercury, silica) in a dilute solution of the desired molecule that bears at one end a group with high chemical affinity for the surface (i.e., a sulfide or disulfide for the coinage metals) and the chromophore at the other.[24] It is now well-known that the resulting monolayers are highly ordered, or even crystalline, and are blocking toward electron transfer to redox couples present in a contacting electrolyte solution.[25] They exhibit surface properties consistent with an oriented positioning of the terminal group.[26]

Surface aggregation is affected strongly by molecular structure and by the ease with which neighboring molecules can pack into an arrangement that resembles the solid-state unit cell. Because of difficulties associated with producing a flat, defect-free, and step-free surface by chemical or evaporative deposition of the contacting metal, local domain formation is often observed.[27] Some adsorbates are bound to different areas of the surface (e.g., on steps, edges, or flat surfaces) and are therefore more easily displaced than others. By repeated washings and exchanges, however, it is possible to produce a surface in which only the dominant highly oriented surface is probed.

To exemplify these principles, we have prepared a self-assembled monolayer in which a *cis*- or *trans*-stilbene group is present at the outside of a SAM.[28] When the stilbene bears a cyano group, as in **7**, the surface hydrophobicity differs significantly in the two isomers. A molecular mechanics calculation shows that in the trans isomer, the cyano group protrudes into the contacting solution, providing an accessible hydrogen bond acceptor site and producing a hydrophilic surface characterized by a low contact angle with a sessile water droplet. In the cis isomer, in contrast, the cyano group is buried back into the monolayer, and the surface contact is largely hydrophobic and dominated by the hydrocarbon character of the aromatic ring. The surface energies of these SAMs therefore differ, and the differential affinity for a contacting water droplet produces an effect observable even to the naked eye.



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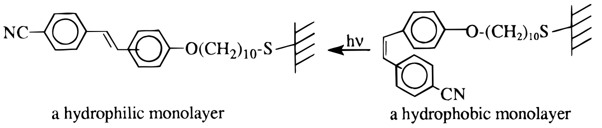
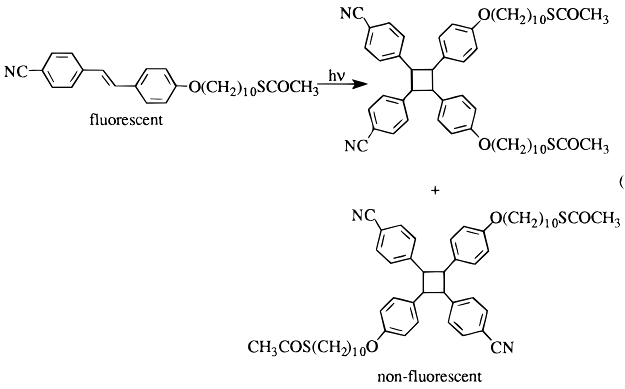
A significant scientific question related to the photoreactivity of a chromophore attached as a SAM is whether the metal's continuum of electronic states would effect an immediate excited-state quenching, as has been observed many times with organic molecules chemisorbed or physisorbed directly onto metallic surfaces.[29] Grazing angle fluorescence measurements, however, indicate that excited states of probe molecules present in a SAM that has alkyl linking chains longer than about five atoms are not appreciably quenched by through-bond coupling with the metallic surface.[30] A comparable result has been described by White and co-workers in their study of photoreactivity of simple organic molecules on metallic surfaces.[31] Such photophysical studies can provide an interesting vehicle for understanding through-bond electronic coupling through linker chains of varying chemical composition.

Photoexcitation of a cis monolayer produces a geometric isomerization to the trans isomer, with an accompanying change in contact angle, eq 1.[28] When the irradiation is accomplished through a mask, surface photopatterning is accomplished. Thus, this photoreactivity can be monitored by "developing" an exposed plate by condensing water droplets by cooling the plate in an atmosphere of moist air. This technique therefore constitutes a new method for non-silver-based imaging with a resolution comparable to that imposed by the mask and by the wavelength of the incident ultraviolet light.



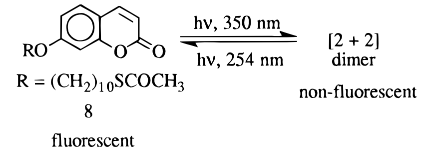
(1)

Continued irradiation of stilbenes as concentrated solutions or in the solid state produces a [2+2] photodimerization in which the olefinic bonds between the phenyl rings bind into a cyclobutane, eq 2.[32] This photodimerization removes conjugation and thus extinguishes the weak fluorescence observable with the parent stilbene SAM. When this same reaction is conducted as a thiol-bound monolayer on gold, surface-patterning by fluorescent and nonfluorescent regions is attained. In this way, the photodimerization leads to permanent photoimaging, exhibited by both photochromism and differential surface emission.



(2)

Other photoactive groups also participate in regiocontrolled photoreactions when disposed as self-assembled monolayers. As in the photodimerization of stilbene, a [2+2] cycloaddition of an appended coumarin **8**, eq 3, produces a photochromic effect as well as fluorescent switch.[33] With coumarin, however, the cyclobutane dimer can be cleaved upon photoexcitation at more highly energetic wavelengths. Thus, the fluorescence of the parent coumarin can be extinguished by photolysis at 350 nm, but restored by later irradiation at 254 nm. This cycle thus constitutes a reversible imaging technique, controllable in both directions by wavelength-specific photolysis.



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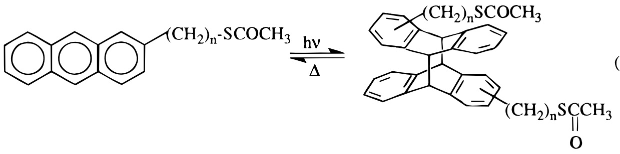


(4)

Similarly, with an appended anthracene, photoinduced dimerization takes place at the 9,10-positions of the ring, eq 4.[34] Although the thermal and photochemical reversibility of anthracene photodimerization has been reported in solution, partial degradation takes place upon repeated cycling of this SAM. The cause of this photodegradation has not been unambiguously assigned, but it likely derives from oxidative destruction caused by trace amounts of oxygen contained within the deposited layer.[35,36] So little material is involved in the formation of a SAM that the usual techniques used by photochemists for deoxygenation appear to be inadequate for full protection against this competing degradation pathway, although recent results with photoactive materials bound to colloidal gold suggest that analogous photochemical conversion can produce stereoselectivity and regioselectivity not easily attainable in homogeneous solution.

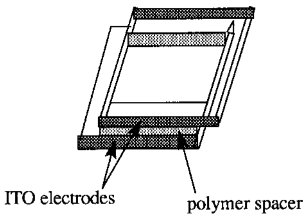
C. Controlling Vectorial Electron Transfer

Given that several quite different synthetic methods are now available for precise positioning of an array of chromophores along a spatially defined support, the next level of complexity encountered in building an optoelectronic device is to define an energetic ordering of the appended electron or energy relays so that the direction of charge carrier or exciton migration can be specified.

1. Redox Gradients in Block Copolymers. The simplest means for attaining directional electron transfer is to assemble a series of groups with ordered oxidation or reduction potentials as in **1**, where the redox potentials for the appended groups are ordered monotonically as a result of the sequential binding of the desired monomer during block copolymerization. The proof-of-concept for directional electron transfer has been made in many model systems that seek to mimic photosynthesis. For example, the impressive arrays of triads, tetrads, and pentads prepared by Gust and Moore have shown that small incremental energy steps provide effective channels for electron migration, while suppressing back electron transfer.[37]

The block copolymers whose syntheses were described in the previous section provide just such a gradient.[12−19] Thus, an exoergic energy cascade (from left to right, as written above for polymers **1** and **3**) exploits the spatial ordering built into the molecule during synthesis. Here an electron hops, in sequential steps, from an appended donor chromophore (often in its excited state) through a series of acceptors that possess orbital vacancies at lower and lower energies. As long as one end of the polymeric chain is specifically functionalized for attachment to a surface, perhaps with the groups described for producing SAMs, then nonrandom charge migration is observed.

2. Directional Charge Carrier Transport through Photoconductive Layers. The direction of charge carrier mobility can also be controlled in a solid-state sandwich electrochemical cell **9** by applying a potential difference between the anode and cathode, as long as the intervening material can transport charge. If the material is photoconductive, a solid-state photovoltaic device is produced.[38] In the latter cell, the separated charges can be trapped by extinguishing the light source, thus producing an optoelectronic signal that can be read amperometrically or coulostatically.[39] The resolution attainable in the resulting images is limited by the pixel size of the unit cell containing the separated charges,[40] which can be quite small (<50 nm).



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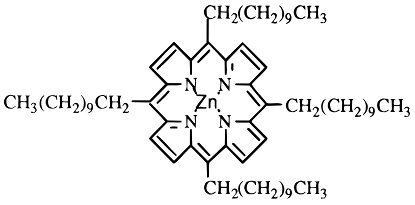
In collaboration with Bard and co-workers at the University of Texas, our research group has shown that several new series of dyes, e.g., porphyrin **10**, can function effectively as just such a material.[41] Because of strong, long-range electronic interactions along the stacking axis of these low molecular weight compounds, electron mobilities over many nanometers are observed.[42] Although these materials sometimes possess stable liquid crystalline phases, this property is not necessary for photoconductivity,[43] although it does ease the fabrication of the cell. Simply by melting the photosensitive compound to an isotropic melt which capillary-fills the preassembled sandwich cell **9** and cooling it through its liquid crystalline phase to produce an ordered solid film, the nanoscopic order required for long-distance charge carrier migration is attained. Time-resolved microwave conductivity measurements similarly indicate that local order in the liquid crystalline or solid phases significantly affects charge carrier mobility.[44] Recent advances in understanding light-emitting diodes[45] and molecular field effect transistors[46] similarly rely on quite analogous photoinduced charge transport phenomena.



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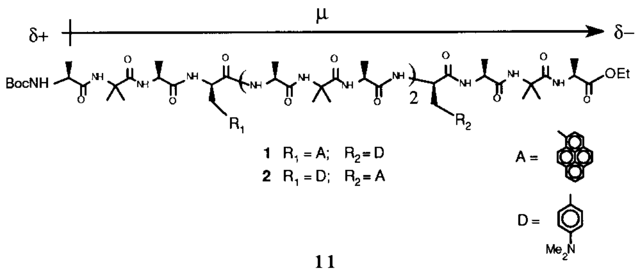
D. Spatial Differentiation through Environmental Effects

Finally, we have shown that the external electrical fields felt by a charge carrier as it moves along a given migratory pathway significantly influence its directional mobility. A range of biological effects have been rationalized by analogous field effects,[47] and in large part, this effect may be responsible for the preferred direction of electron migration in the otherwise C-2 symmetric photosynthetic reaction center.[48]

Specifically, a substantial field is generated by the accumulated macroscopic dipole associated with the directionality of the oriented peptide bonds pointing along the helical axis in a [3,10]- or α-helix of a photolabeled polypeptide.[49] More than order-of-magnitude differences in electron-transfer rate are observed along the α-helix in peptides **11**, in which identical groups are appended at identical positions, differing only in the direction of the D−A interaction, which is aligned with or against the helical dipole.[50]

Calculations show that the basis for this rate difference is rooted in redox potential differences associated with charge centers near the termini of the electrical vectors.[51,52] Furthermore, disruption of the helix by including guanidinium as a hydrogen bond competitor or by



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including helix-disruptive amino acid residues causes this effect to disappear.[53] It is likely that analogous electrical fields may also influence the facility of electron transfer in functionalized polynucleotides, and may be significant contributors to the abnormally small β values observed in DNA segments[54] and in hairpin-turned oligonucleotide double helices.[55]

E. Conclusions

If one is ever to define the fundamental principles governing the functioning of optoelectronic devices, it will be necessary to understand how intramolecular electronic coupling and environmental effects affect charge carrier migration in spatially defined nanoscopic arrays. New synthetic routes make available discrete, rigid, high and low molecular weight compounds useful in such nanoscaled arrays, and recent advances in the formation of self-assembled monolayers provide facile means for the precise positioning of these units onto a defined surface.

Photosensitive groups attached as ω-functionalized appendages onto alkyl chains longer than about six carbons form well-behaved and structurally regular monolayers. Because the excited states of these groups are not fully quenched by the metal support, suitably constructed self-assembled monolayers on gold can be stimulated by light to achieve directional electron transfer that is observable spectroscopically or to induce photochemical conversions that produce unusual visual images. Moreover, since the efficiency of charge migration is significantly affected by an electric field (as in model polypeptides), kinetic control of the observed optical effects by an externally applied potential is likely for many such modified electrode arrays. In addition, the local order afforded by the monolayer or liquid crystal profoundly influences the distances over which efficient charge migration can be observed, which can be quite large on a molecular scale.

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