

Polymeric and Supramolecular Arrays for Directional Energy and Electron Transport over Macroscopic Distances

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Photoinduced electron transfer,¹ one of the simplest conceivable molecular transformations, has profound consequence on reactivity, converting an electron-rich donor molecule D to an electrophilic cation radical and an electron-deficient molecule A to a nucleophilic anion radical (eq 1). Occurring within most branches of



science and in virtually all subareas of chemistry, electron transfer sets the stage for redox reactions which differ significantly from those characteristic of the unactivated precursors. This altered chemical behavior can be exploited, however, only if the oxidized and reduced species persist long enough to participate in secondary reactions. In practice, this is achieved only if the back electron transfer (that regenerates starting materials) is suppressed efficiently.

Control of back electron transfer can be accomplished by exploiting differences in orientation, solvation, and/or thermicity for the forward and reverse transfers.² In addition, many clever schemes have used the molecule's environment to control the directionality of electron transfer.³ For example, the rates of electron transfer in micelles or thin films differ significantly from those occurring with the same reaction partners in homogeneous media. Energy or electron transfer over polymeric arrays might comparably offer improved control of redox-activated reactions.

There are many important practical consequences of long-range photoinduced electron transfer: many photosensitive biological systems, and most proposed light-responsive molecular electronics devices,⁴ operate through photoinduced electron transfer over distances significantly greater than a single molecule. Furthermore, several technological applications require devices employing ordered arrays. For example, molecular shift registers have been described in detail by Hopfield and co-workers,⁵ although the experimental difficulties attendant with the construction of such complex systems have not yet been addressed adequately. Thus, construction of three-dimensional arrays which could control the directional movement of electrons over macroscopically large distances is an important objective for both basic and applied science.

Marye Anne Fox was born in Canton, Ohio in 1947. She received a B.S. from Notre Dame College and an M.S. from Cleveland State University before receiving her Ph.D. from Dartmouth College in 1974. After a postdoctoral stay at the University of Maryland, she joined the faculty at the University of Texas at Austin where she occupies the M. June and J. Virgil Waggoner Chair in Chemistry. A former director of the Center for Fast Kinetics Research at the University of Texas, she is currently a member of the National Science Board. Her principal research interest is physical organic chemistry.

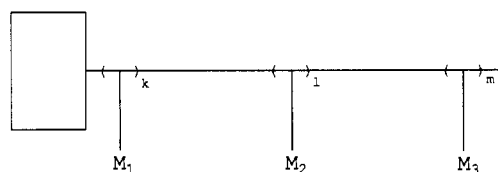


Figure 1. A polymeric array for directional electron or energy transfer.

For several years, our research group has focused on methods to prepare and characterize supramolecular (often polymeric) arrays capable of spatial exploitation of the charge separation induced by light absorption. A prototype of the system we seek to prepare is shown in Figure 1. Here, three macroscopically separate blocks in a polymeric array are arranged sequentially along a backbone whose terminus is chemically bonded to a fixed probe. The component units of each of these blocks would themselves be photoactive or electroactive and would be arranged along an increasing or decreasing energy gradient so as to provide an anisotropic driving force for charge separation.

These components should also be easily accessible, but capable of modification so as to define a graded property. For example, the observed voltammetric peak potentials for the one-electron reduction of a series of N-alkylated nicotinamides vary by more than 1 V depending on whether the group bound to the ring nitrogen is alkyl, a proton, or perfluoroalkyl.⁶ With these units attached as pendant groups on a polymer chain in a geometry permissive of unit-to-unit interaction and arranged according to increasing or decreasing peak potential, a gradient for directional electron transfer would be established (Figure 2).

A similar series of structurally related dyes graded for energy transfer can be seen in compounds 1-3.⁷ Upon successive condensations with maleonitrile, a commercially available oxocarbon dye (1) can be transformed to 2-4, with extended conjugation and a red-shifted absorption maximum accompanying each additional condensation. The arrangement of 1-4 sequentially along a backbone as discussed above would result in a

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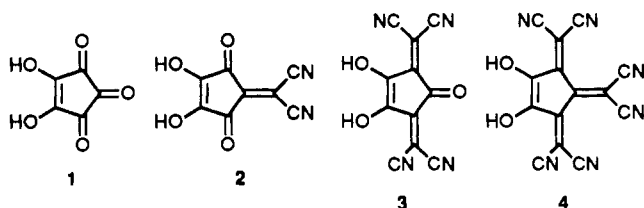
(3) Fox, M. A. *Top. Curr. Chem.* 1991, 159, 68.

(4) Lupinski, J. H.; Moore, R. S., Eds. *Polymeric Materials for Electronics Packaging and Interconnection*, Symposium Series 407; American Chemical Society: Washington, DC, 1989.

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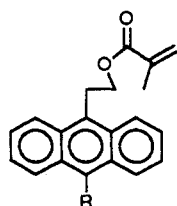
graded array for energy transfer. Compound 2, for example, could transfer to 3 in a thermodynamically allowable manner, but transfer in the opposite direction (to 1) would be thermodynamically impermissible. In parallel to the directional electron transfer expected among redox-active nicotinamides, sequential attachment of blocks of three of these molecules would allow energy migration to occur over macroscopic distances and in only one direction.

The practical construction of such an array requires that several significant problems be solved. Among these are (1) controlling energy or electron transfer within a homofunctionalized block, (2) defining whether the orientation of the active components within a block must be critically controlled, (3) optimizing electron or energy migration across the interface between blocks, (4) developing a synthetic methodology for the assembly of the polymeric array, and (5) establishing a method for reliable attachment of one end of the polymeric array to a probe (most conveniently, a metal or semiconductor electrode) in order to define the source and sink for excitation or electrons.

None of these problems is trivial: each in itself merits continued and extensive investigation. The remainder of this Account will provide examples of how each of these component problems has been addressed in our group.

Energy Migration within a Photoresponsive Homopolymer

For optimal energy transfer through a homopolymeric block to be achieved, the factors which influence chromophore–chromophore interactions between pendant groups poised along a polymer chain must be identified. In order to probe whether the structure of a component chromophore can significantly influence the magnitude of interaction with its nearest neighbor in a homopolymer, a probe molecule employing a functionalized anthracene was prepared. Anthracene was chosen as the probe since its photophysical properties had been previously well characterized.⁹ Through a β -hydroxyethyl substituent bound at the 9-position, a derivatized anthracene can be tethered to methacrylic acid to form a polymerizable ester 5. When polymer-



5: R = H, alkyl

ized, this repeat unit maintains the electronic isolation

(8) Fox, M. A.; Britt, P. F. *Photochem. Photobio.* 1990, 51, 129.

(9) For example, see: Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley Interscience: London, 1970.

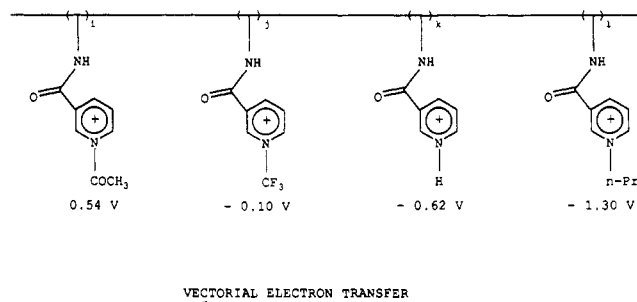


Figure 2. A multicomponent redox relay system based on functionalized nicotinamides.

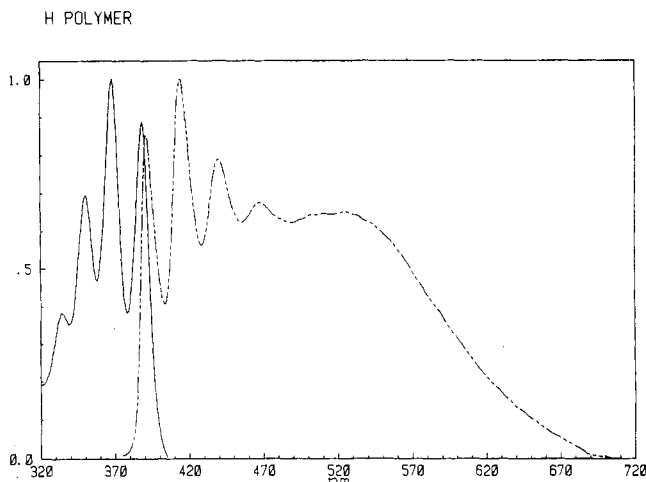


Figure 3. Absorption (—) and emission (---) spectra of poly(2-(9-anthryl)ethyl methacrylate).

of the pendant anthryl groups and thus helps to assure high photochemical stability in the functionalized polymer. Since conditions for polymerization of methacrylic esters are known, parallel routes for the preparation of this anthryl-functionalized polymer could be conveniently employed.¹⁰ The tethered anthryl group at the 10-position could also differentiate a series of sterically related chromophores.¹¹

The magnitude of interchromophoric interaction between anthryl residues along the homopolymer chain can be gauged by the intensity of the characteristic excimer emission.¹⁰ A comparison of the absorption spectrum of the parent compound (R = H), either as a thin film or as a dilute ethanolic solution of a homopolymer of molecular weight $\sim 50\,000$, shows a mirror-image relationship between each of the absorption and emission bands, but with an additional strong, broad band at ~ 516 nm characteristic of anthracene excimer emission (Figure 3).¹⁰ The intensity of this fluorescence is strongly attenuated by placing sterically blocking substituents at the 10-position, as can be seen in the corresponding emission spectrum of the analogous polymer bearing an isopropyl group (Figure 4). That excimer formation has been attenuated, rather than obviated, can be seen from a comparison of the spectrum of the 10-alkylated polymer with that of a dilute solution of the corresponding monomeric pivalate ester.¹¹ A more detailed kinetic and photophysical study confirms these qualitative conclusions. Thus, the magnitude of chromophore-to-chromophore interaction can be controlled by synthetic manipulation of the substituent at C₁₀, which controls the approach of the interacting

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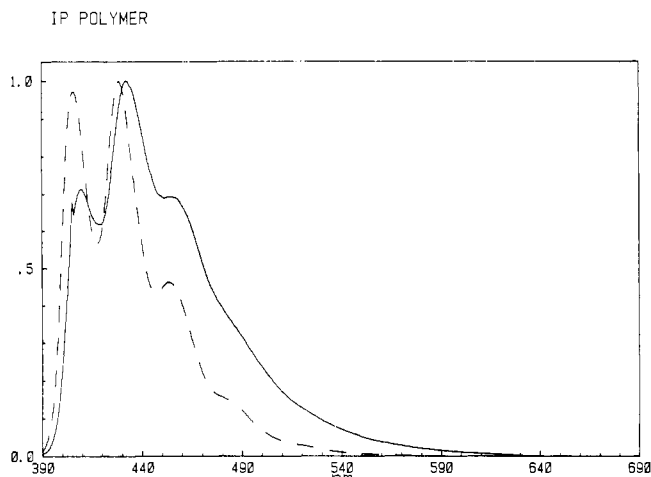
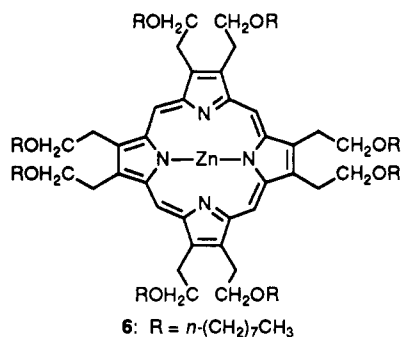


Figure 4. Emission spectra of 2-(10-isopropyl-9-anthryl)ethyl acrylate (—) and 2-(10-isopropyl-9-anthryl)ethyl pivalate (- - -).¹¹

chromophores pendant along the functionalized polymer chain. Such energy transfer is usefully employed in the photosensitization of semiconductor electrodes by thin films of polymers of 5.^{12,13}

Orientation of Interacting Groups

Orientation is known to influence significantly the efficiency of intramolecular electron transfer in many systems,¹⁴ but to our knowledge detailed orientational studies in homopolymeric arrays have not yet been reported. As a model system for such arrays, we have investigated the photophysics of a self-assembling liquid crystal which forms an oriented discotic mesophase (stacked columns) upon heating to modest temperatures.¹⁵ This material 6 is prepared by symmetrical



functionalization of the β -carbons of a porphyrin with eight long-chain aliphatic groups.¹⁶ The metalated porphyrin core is rigid and planar, allowing for effective π -stacking, while the floppy peripheral side chains introduce a proclivity for liquid crystallinity^{16,18} (Figure 5). As a result, it is possible to prepare large-area, anisotropically oriented thin films in which defects or structural irregularities produced during film formation are self-healed. The existence of π -stacked oriented arrays is signaled not only by the presence of phase transitions observed by differential scanning calorim-

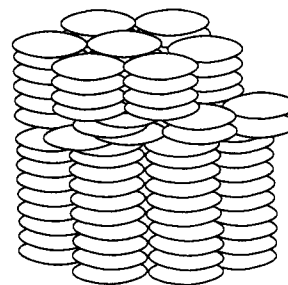


Figure 5. An artist's view of order in a discotic mesophase.¹⁷

etry but also by a spectroscopic signature in its absorption spectrum for the enhanced order accessed in the ordered liquid crystalline mesophase.¹⁵

After capillary filling of a thin film of this liquid crystal between two conductive indium tin oxide electrodes, supramolecular order is maintained as the film is cooled to the solid state. With this orientation, it is possible to produce a photovoltaic device for sustained current production.¹⁹ Such a device functions efficiently because of different rates for electron and hole injection at the illuminated and dark electrodes, as well as photoenhanced conductivity ($>10^6$ times higher than in the dark) in the bulk of the thin film. Since dark- and light-induced conductivity through such π -stacked arrays are regulated by film order, this device depends on efficient communication between the layered, oriented molecules. The magnitude of the efficiency of charge transfer across this array depends on the degree of orientation of the thin film,²⁰ implying again that orientational control will be important in designing polymeric arrays for charge separation across macroscopic distances.

Charge Transfer across Blocks

Once it is possible to generate blocks in which steric and orientational interactions between redox-active groups within the individual blocks are effectively addressed, factors influencing the efficiency of electron transfer between blocks must be identified. This problem can be effectively modeled with chemically different thin layers whose conductivity can be switched individually by an external method. This goal can be attained by preparing conductive bi- and trilayered polymers of ordered composition. For example, the electropolymerization of pyrrole or of thiophene on a metal electrode forms a layer whose thickness can be controlled by judicious coulometric control during electrooxidative polymer deposition.²¹ Growth can be disrupted and then continued at a later time, perhaps after changing the contacting monomer, specifically because these polymers can be cycled potentiostatically from an insulating to a conductive state. By changing the composition of the monomer feed, it is possible to build structures which are discrete bilayers,²² films of constant mixed composition, or films with spatially graded composition²³ (Figure 6).

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(21) Skotheim, T. A., Ed. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986.

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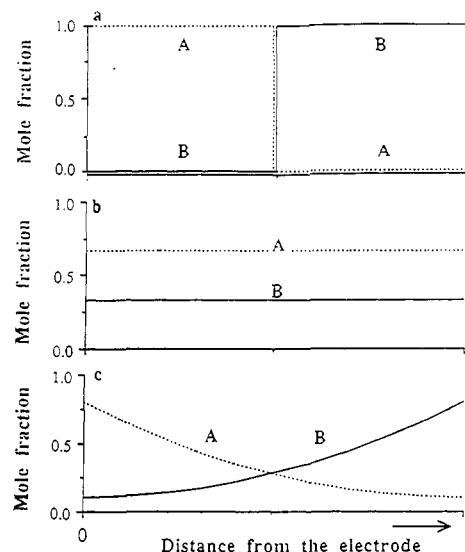


Figure 6. Structure in conducting copolymers of constant overall composition as (a) sequentially deposited layers, (b) copolymer of constant mixed composition, and (c) monotonically graded composition.²³

These bilayer electrodes can be used as charge rectifiers. We have shown, for example, that if micron-thick bilayers of polypyrrole and polythiophene are deposited on a metal electrode, the order of deposition governs the efficiency of charging or discharging of the outer layer.²² Since polypyrrole is oxidized at a less positive potential than polythiophene, a layer of polypyrrole intervening between a metal and an outer polythiophene layer can be made conductive before the potential is reached for oxidation of the outer layer. That these bilayers can act as an electrical switch can be demonstrated by the contrasting shapes of cyclic voltammograms of the two possible ordered arrays (i.e., by monitoring current flow induced by scanning reversibly from negative to positive potentials). A metal-polypyrrole-polythiophene bilayer shows a cyclic voltammogram which resembles the superimposition of those for polypyrrole and for polythiophene on the metal (Figure 7a). When the order of attachment is reversed, however, a suppression of the oxidation wave for the outer layer occurs because of the insulation of the inner polythiophene layer at potentials where polypyrrole would itself be oxidized (Figure 7b). As a result, the wave at +1.0 V observed in Figure 7a is absent in the oppositely ordered bilayer in Figure 7b. That charge is stored in the outer layer (after oxidative cycling of the inner layer) is obvious from the lower current density observed on a second cyclic voltammogram. Upon reversal of electrode charging, charge is drained from the inner polythiophene layer, making it insulating, at a potential less cathodic than is required to convert the outer polypyrrole layer to its insulating state. The charge trapped in the outer layer can be discharged at a later time by interaction with a solution-phase redox reagent.

That such effects derive from the spatial organization of the bilayer can be demonstrated from the contrasting cyclic voltammogram behavior obtained either in a random copolymer of these two components or in a graded layer in which spatial resolution between charge trapping polymeric components is minimized.²³ These studies affirm that controlled spatial deposition of polymeric layers allow for electronic charge motion over micron distances, with trapping occurring within dif-

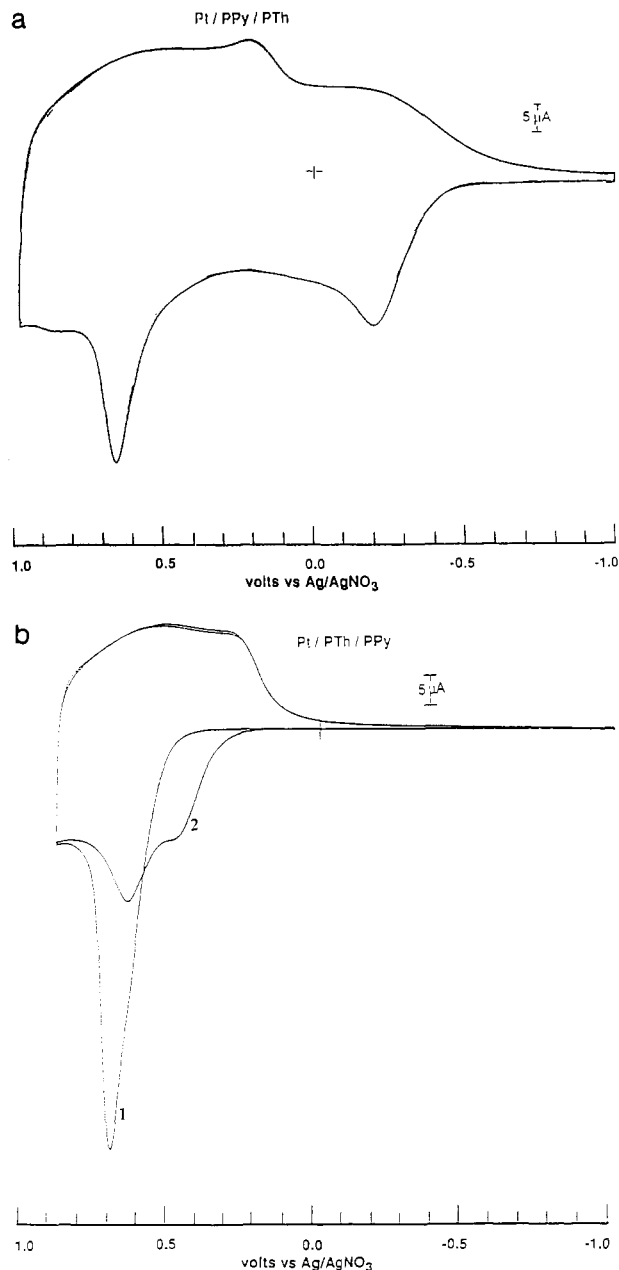


Figure 7. Cyclic voltammograms of conducting polymer bilayers: (a) Pt-polypyrrole-polythiophene; (b) Pt-polythiophene-polypyrrole.²²

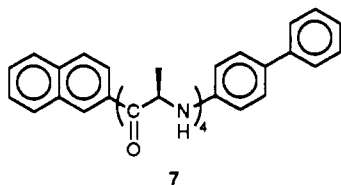
ferent blocks. Thus, directional motion of charge through spatially anisotropic^{24,25} layers is possible and must occur efficiently for practical applications of vectorial energy or electron transfer.

Synthesis of Spatially Controlled Assemblies with Graded Properties

After the problems associated with optimizing excited-state or electron-transfer interactions between functionalized groups within an oriented block and across the interface by two blocks have been solved, synthetic methods to assemble redox-active blocks in a polymeric array will be needed. A likely solution to this challenge can be found in the many new exciting developments in polymer chemistry recently described for sequential deposition of monodisperse blocks along a polymer chain employing radical, anion, cation, group

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with the alanines, however, greatly enhances solubility while simultaneously stabilizing a [3,10] helix.²⁹ That a helical structure has been attained when including 10 amino acids along the chain can be shown from the contrasting intensities for an intramolecular charge transfer band, a conclusion that can be confirmed by either circular dichroism or NMR spectroscopy. When dimethylalanine and pyrene are appended to an oligopeptide one unit too short for [3,10]-helix formation, exciplex emission is observed which is absent in the same oligopeptide with one additional aib unit (Figure 8). Inclusion of a specifically ordered redox-active side chain along this [3,10]-helical backbone should allow for sequential electron transfer migration down a single rigid chain. Such studies are in progress.

Anchoring the Polymeric Chain to a Surface

The attainment of macroscopically directional electron transfer along a functionalized polymer array requires that one end of the polymer be differentiated from the other. This is easily achieved if one end is anchored to a fixed probe site (Figure 1). The by-now well-recognized affinity of disulfide and thiol linkages³⁰ for gold makes the chemisorption of functionalized alkyl thiols a convenient method for specifically binding one end of a functionalized array to an electrochemically addressable probe. Thus, with the first block of a multiblock graded polymer functionalized with a thiol-rich region, covalent attachment, perhaps through a mixed monolayer, can occur. The close packing which leads to self-assembled monolayers in simple long-chain alkyl thiols is unlikely to produce control of surface orientation in these macromolecules. It is therefore important to establish whether functionalized long alkyl chains, as crude models for the surface packing of the polymers we seek, can preserve orientation and kinetic stability at sub-monolayer coverages.

We have recently shown that several mixed monolayers on gold can exchange long-chain alkyl thiols terminated by a redox-active group, producing two separately addressable microdomains on a gold surface (Figure 9).³¹ Thus, a mixed monolayer of redox-active (e.g., an alkanethiol bound to a ferrocenyl or acylferrocenyl group) and redox-inactive (e.g., an alkanethiol) materials selectively exchanges with about a third of the redox-active sites over a period of several hours.³² Resoaking of this bifunctionalized surface in a solution containing a second redox-inactive long-chain alkyl thiol displaces the exchanged component, while leaving the first nonexchanged material in a kinetically stable environment. Possible sites for the "defects" at which

EXCHANGE OF ALKANETHIOLS AT DEFECT SITES

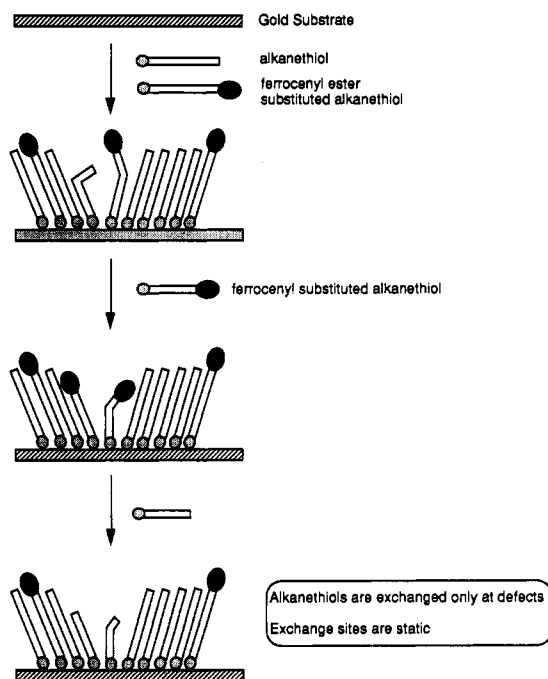


Figure 9. A model for two kinetically differentiated populations formed by self-assembly on a smooth gold surface.³²

this exchange can occur can be surface irregularities, metal steps or edges, or inhomogeneities between tilted self-assembled arrays. Thus, alkyl thiol groups on gold are useful not only as anchoring agents for specific introduction of sub-monolayer concentrations of thiol-terminated macromolecules but also as a two-dimensional surface for the construction of nonhomogeneous arrays.

Concluding Remarks

Controlled electron and energy migration in asymmetric nonhomogeneously dispersed environments is important in understanding the function of many biological systems and in developing the next generation of molecular photonic materials. A scholarly study of the scientific basis of this problem poses a tremendous intellectual challenge requiring significant expertise in organic synthesis, photophysics, polymer chemistry, organic electrochemistry, and materials characterization. Such investigations provide exquisite examples of how advances in fundamental aspects of classical physical organic chemistry (structure-activity relationships) are absolutely necessary if the practical, technological applications of such materials are to be realized.

I am particularly grateful to my talented co-workers who conducted the experiments described here (Phillip Britt, Russell Seguin, Prashant Kamat, Brian Gregg, Hong-long Pan, Walter Torres, Mark Meier, Craig Wall, Stephen Creager, and David Collard) and to Traci Batchelder, Diana Watkins, and Wayne Jones who are continuing the group's effort in this program. This work was sponsored by the U.S. Department of Energy, Fundamental Interactions Branch of the Division of Chemical Sciences, Office of Basic Energy Sciences.

Registry No. 5 (R = H) (homopolymer), 129572-21-0.

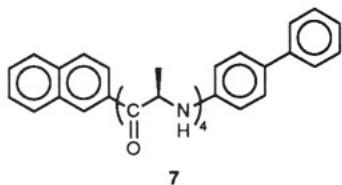
(28) Wall, C. G.; Healy, E. F.; Fox, M. A. *Int. J. Quantum Chem.* 1992, 44, 543.

(29) Li, T.; Budt, K. H.; Kishi, Y. *Chem. Commun.* 1987, 25, 97.

(30) Bain, C. D.; Troughton, E. B.; Tao, Y. T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* 1989, 111, 321.

(31) Collard, D. M.; Fox, M. A. *Langmuir* 1990, 6, 1617.

(32) Collard, D. M.; Fox, M. A. *Langmuir* 1991, 7, 1192.



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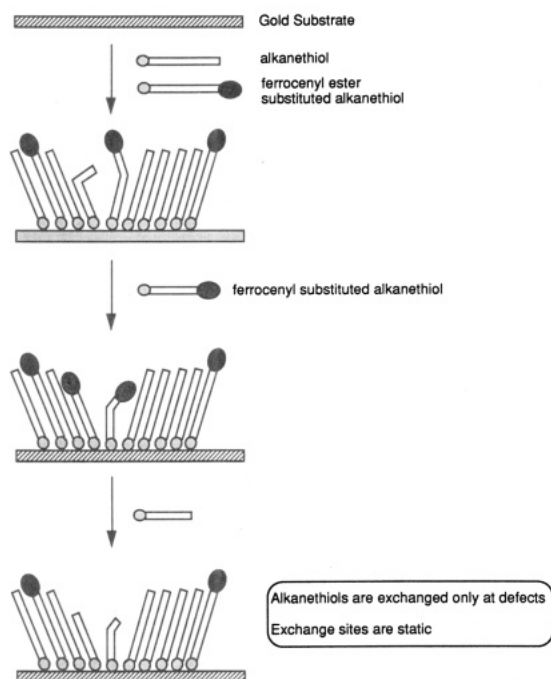


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