Anisotropic energy and electron migration in multichromophore-laden polymers on metal surfaces

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Abstract: Anisotropic orientation of chromophores on metals and metal oxide surfaces can be attained by self-assembly of oriented dyes bearing appropriate surface recognition functionality. For example, chromophore-laden polymers can be bound to gold either by polymerizing a chosen monomer onto a surface-bound trithiol "seed" or by direct binding a pre-formed organic polymer terminated with a thiol functional group.

Efficient light harvesting is accomplished when multiple chromophores are covalently attached to one or more segments of a multiblock copolymer. Photophysical measurements of exciton mobility and of electron transfer efficiency will be described, along with the effect of molecular architecture on the suppression of charge recombination via back electron transfer.

Introduction

Practical optoelectronic devices often require absorptive dyes to be anisotropically oriented as a thin film on the surface of a catalyst or a poised electrode. The several techniques now available to achieve this alignment usually rely on weak intermolecular forces that, in sum, result in discrete domains of highly structured materials. These include, for example, aggregates produced as solid single crystals, liquid crystals, Langmuir-Blodgett films, poled polymers, and host-guest inclusion complexes. In addition, it has been shown that exquisitely ordered, tightly packed monolayers can be produced by covalent attachment of long chain alkyl thiols to gold, silver, and other metals (1) or by chemical bonding between metal oxides with long chain organic isocyanides or trialkylsilanes (2).

By using similar surface chemistry, we have been able to attach organothiols to a metal (typically gold) surface for one of two purposes: (a) as a seed site for the growth of oriented polymers; or (b) as an attachment site for anchoring pre-formed polymers onto a metal surface. We have then used spectroscopy to define the anisotropic orientation of absorptive dyes attached along the appended polymer chains. Here, we discuss the chemical composition of these oriented polymers and how photophysics can be employed to establish the directionality of energy migration and of photoinduced electron transfer along the rigid backbones attained in these synthetic polymers.

Directionally Aligned Helical Peptides

With an aminotrithiol **1** as surface seed, we have grown α-helical polyalanine to micron thicknesses (3), as established by grazing-angle Fourier transform infrared spectroscopy. The tripod anchoring was required because the interatomic spacing on the Au [100] surface (4.1 Å) is shorter than that required by the diameter of an α-helix. Treatment of this modified surface with the *N*-carboxyanhydride of a desired amino acid results in the growth of a layer of peptide. The degree of helicity of the resulting layer was established by the extreme narrowness of the amide I and II infrared bands. The relative intensities of the amide I infrared band when detected using alternately perpendicularly and horizontally polarized light on indium tin oxide-float glass indicates that the direction of the helix is roughly normal to the surface (the glass surface was examined because the horizontal components of the infrared bands are inactivated by a metallic conductor surface such as gold).

This method can be extented to the preparation of helical polypeptide layers derived from amino acids with larger side chain groups than the methyl group of alanine. To accomidate the larger cross-sectional area required by larger polypeptides (e.g., polyphenyl alanine and polyleucine) the seed sites were modified by formation of a double layer of the aminotrithiol **1**.
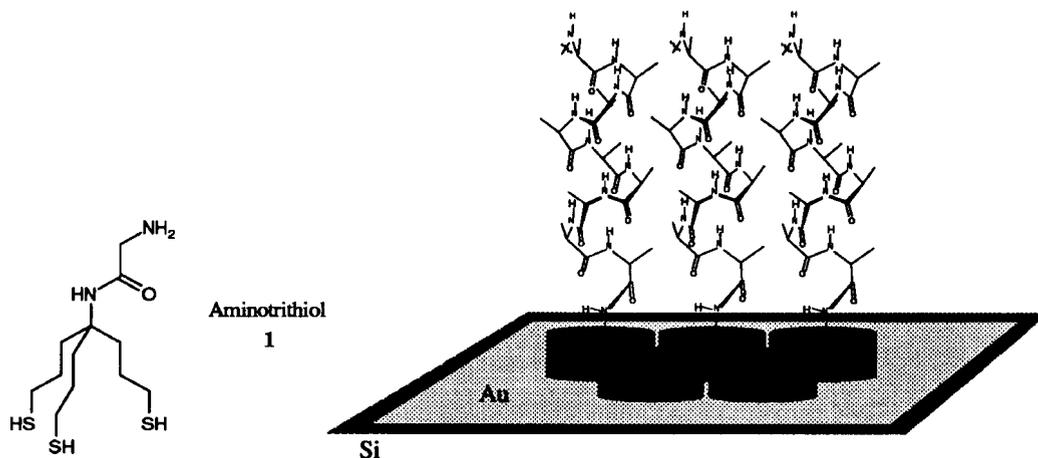
Schematic representation of helical polyalanine grown from aminotrithiol **1** attached to a gold surface.

Such films are interesting in their own right, but especially because they provide for an oriented net macroscopic dipole resulting from the sum of the electrostatic contributions of the individual constituent amide groups (3).   This helical dipole induces a local electrical field that significantly influences the magnitude of the rate constant for electron transfer between groups attached to the chain (4).   For example, in peptides **2** and **3**, the rate constants for photoinduced electron transfer from the pendant dimethylanilino

2 R_1 = A; R_2 = D
3 R_1 = D; R_2 = A
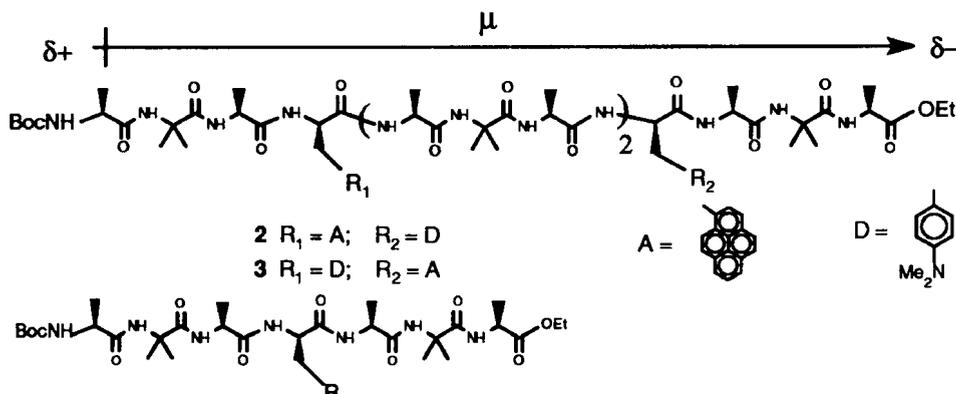
group to the excited pyrenyl group differ by more than an order of magnitude at -45° (5).   Analogous non-centrosymmetric orientations have been shown earlier to also have profound effects on solid state organization (6) and on molecular crystal engineering by shape mimicry (7).

Photophysics as a Means to Establish Conformational Rigidity

Because our ultimate goal is the use of such oriented polymers as platforms for long distance electron transfer, we have prepared a series of conformationally rigid macromolecules that bear light-responsive dye side chains. Our hope was that such compounds would provide a vehicle to efficiently harvest light while simultaneously acting as conduits for energy migration and long distance electron transfer (8). Steady state and time-resolved photophysics would be employed to demonstrate vectorial exciton migration over a synthetically defined energy gradient. We describe here three types of polymeric backbones appropriate for studying such effects: hydrocarbons with alternating rings and multiple bonds bearing chromophores through pendant acetal or ketal linkages, functionalized poly(isocyanides), and aryl substituted poly(acrylates).

These macromolecules must permit: (a) synthetic definition of the orientation and spacing of the absorbers, relays, and quenchers along the polymer backbone; (b) a method by which the mechanism and rate of energy and electron transfer through a homopolymeric block (through-space or through-bond) can be established; (c) a technique to demonstrate optimization of energy or electron transfer across the interface between blocks; (d) a means for the confident suppression of energy-wasting back electron transfer by charge recombination; and (e) a structural basis for the expected inhibition of energy-dissipative excimer or exciplex formation. They must as well be easily accessible by synthetic routes that allow for low polydispersity (controlled molecular weights) and for the introduction of several functionalized monomers as component blocks, a goal best attained through living polymerization.

Block Copolymers Prepared by Ring Opening Metathesis Polymerization

Extended block copolymers constructed from conformationally restricted hydrocarbon backbones can be produced by ring opening metathesis polymerization (ROMP) (9). Such backbones are functionalized by assembly of a series of site-specific chromophores and quenchers previously established to participate in long distance photoinduced electron transfer. With such substrates, we can probe energy migration through a series of relays until an exciton is localized at a block interfaces, where interfacial electron transfer produces a spatially separated ion pair (10). With variable experimental conditions (temperature and solvent), specific excited states can be monitored and the rates of energy migration and of electron transfer established.

These ROMP copolymers can contain an indefinite number of blocks. That shown here as triblock **4**, where D designates an electron donor, A an electron acceptor, and R an electron transfer relay represents a typical structure. In this triblock, the subscripts x, y and z define the number of repeat units in each block, which can be varied to define the distance between the donors and acceptors. The unidirectionality of electron transfer shuttling is insured by the difference (a positive driving force) in the respective oxidation and reduction potentials of the donor and acceptor.

Five kinds of photophysical measurements can be made with these substrates (11): (a) energy migration kinetics in the homopolymers and diblock copolymers; (b) solvent effects on exciplex emission in the diblock copolymers; (c) temperature effects on fluorescence and phosphorescence emission in the diblock copolymers; (d) steady-state and time resolved emission on the triblock copolymers as a function of relay length; and (e) transient absorbance and photoinduced charge separation in the triblock copolymers as a

e⁻ transfer
→

$E_{1/2}$(Donor) > $E_{1/2}$(Relay) > $E_{1/2}$(Acceptor)

4
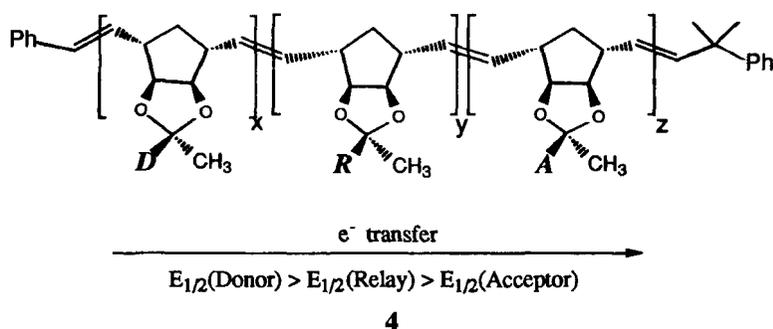
function of relay length. Similarly, energy transfer can be defined either by fitting the rise times for emission in the chromophore-and-quencher labeled diblock copolymers or by comparing rates of Stern-Volmer fluorescence quenching of the homopolymers with those of the component monomers.

Diblock copolymers (**5 a-d**) each bear an additional 50-unit block of photophysically inactive phenyl-appended monomer units to insure complete initiation of all the catalyst prior to addition of a second block, thus serving to maintain a narrow polydispersity and guaranteeing the uniformity of the projected distance for energy or electron migration. The time-resolved emission of the monomers **6 a-c** and their homopolymers **7 a-c** displayed single exponential decay curves with excited-state lifetimes of 8.2 ns, 16 ns and 4.2 ns for naphthalene, phenanthrene, and anthracene, respectively (11).

6a, S = 2-naphthyl
6b, S = 3-phenanthryl
6c, S = 2-anthryl
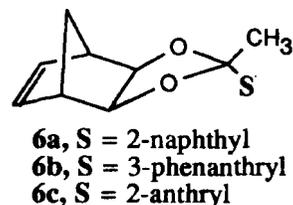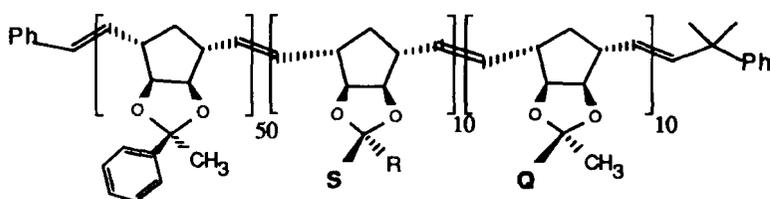
5a, S = 2-naphthyl, **Q** = 3-(*N,N*-dimethylamino)phenyl, **R** = CH₃
5b, S = 3-phenanthryl, **Q** = 3-(*N,N*-dimethylamino)phenyl, **R** = CH₃
5c, S = 2-anthryl, **Q** = 3-(*N,N*-dimethylamino)phenyl, **R** = CH₃
**5d, S** = 3-phenanthryl, **Q** = (2,5-dicyanophenyl), **R** = H
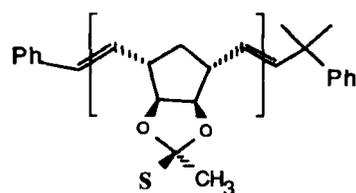
7a, S = 2-naphthyl
7b, S = 3-phenanthryl
7c, S = 2-anthryl

From the slow risetimes observed in their transient emission spectra, we conclude that energy migration between pendant aromatic groups in the copolymers 5 is rather slow (11). Low temperature spectra of these polymers show complete quenching of exciplex emission, presumably because conformational rigidity of the chromophore and quencher at the interface. In the corresponding solution phase spectrs, increased solvent polarity significantly affects the efficiency of exciplex emission in diblocks 5a and 5b, stabilizing the polar exciplex and quenching its emission by 50%. Steady-state and transient emission spectra in this series show that the quantum yield for monomer emission and its fluorescence lifetime decrease with absorber block length, as would be consistent with directional energy migration. Transient absorption spectra indicate that successful charge separation is achieved in these systems, leading to an ion pair whose lifetime depends on the separation between the donor and the acceptor blocks.

The ROMP synthetic route provides a living polymer whose chain growth is terminated either by deprivation of monomer feed or by provision of an effective terminating cap. Homopolymers 7 and block copolymers 5 can be effectively capped with substituted benzaldehydes in which the substituent bears the requisite functionality for surface binding with a metal or metal oxide. The inherent vectorial electron transfer gradient attained in these polymers can thus be transferred to a covalently modified surface in a manner closely resembling that employed for self-assembling monolayers (1,2) or in the *in situ* growth of helical peptides (3).

### Functionalized Poly(isocyanides)

Living polymerization of several isocyanides bearing aryl substituents as chromophores and quenchers can be induced by treatment with nickel catalysts (12). For example, in homopolymers 8 and di- and triblock copolymers 9 and 10, respectively, controllable electron donor and acceptor orientation and spacing is readily attained. These compounds possess helical backbones with a pitch of 4 Å per turn, making non-random directional intramolecular energy migration an effective means to bring an excited state to a block interface where electron transfer quenching of fluorescence (electron transfer from a ground state donor to an excited acceptor) will take place. As with the ROMP polymers, this electronic interaction can proceed either through space (between the two closely spaced arene units) or through the rigid polymer backbone itself.
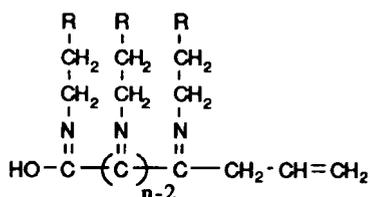
8: R = 2-naphthyl,
   n = 55, 100, 150, or 250
9: R = 9-anthryl, n = 40
1 0: R = 2-phenanthryl, n = 55
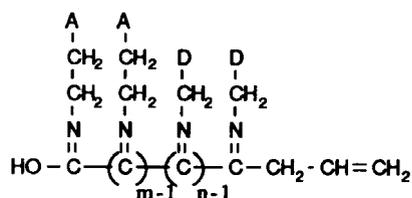
11 : A = 2-naphthyl,
   D = 4-N,N-dimethylanilino,
   m = 160, 80, 40, or 20, n = 40;
   or m = n = 55
1 2: A = 9-anthryl,
   D = 4-N,N-dimethylanilino,
   m = n = 40
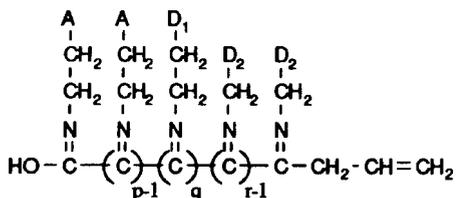
13: A = 2-naphthyl,
   D_1 = pentamethylphenyl,
   D_2 = 4-N,N-dimethylanilino,
   p = r = 40, q = 20 or 40;
   or p = q = r = 100

Steady-state and time-resolved fluorescence spectroscopy show that homopolymers and di- and triblock copolymers 8 - 10 exhibit emission from the isolated chromophores, i.e., naphthyl, anthryl or phenanthryl, upon excitation at 284 or 354 nm (13). As with the ROMP block copolymers, the absence of excimer emission in the fluorescence spectra of all these homopolymers is indicative of a rigid polymeric backbone. In contrast, the diblock and triblock polymers 9 and 10 also emit by energy-dissipative excimer formation, a serious complication in previously described flexible polymeric systems, can be successfully suppressed. Directional singlet energy migration and electron transfer across the block interface is accompanied by enhanced fluorescence quenching in the acceptor-donor diblock copolymers, by inhibition of exciplex formation and an increased fluorescence quantum yield, and by electron transfer evidenced by the transient formation of absorptive radical ion pairs.

Fluorescence quenching in these copolymers takes place through directional energy migration to the acceptor-quencher interface, where the migrating excited state is quenched either by electron transfer or by exciplex formation. An intervening block in triblock polymer **10** comprised of an energy trap whose reduction potential is not aligned with those of the donor and acceptor has the effect of suppressing exciplex formation. Transient absorption spectra of this family demonstrate photoproduction of radical ion pairs, typically with microsecond lifetimes.

Aryl substituted Poly(acrylates)

Methods frequently used to suppress excimer formation in chromophore-laden polymers include the use of bulky substituents (e.g., *tert*-butyl groups) to sterically block the causative inter-chromophore interactions or the preparation of polymers with restricted main-chain flexibility induced by the presence of conformationally constrained rings in the polymer chain. The latter route to backbone rigidity can be accessed in polyacrylates bearing a range of absorptive chromophores. For example, the observed behavior of the polymers obtained from substituted α-methylene-γ-butyrolactones (**11**) and from the cyclopolymerization of substituted diethyl 2,6-dimethylene heptanedioates (**12**), in contrast to that observed for conformationally free linear polyacrylates, attests to the importance of conformationally

11a R = 2-naphthyl   poly(**11a**)
11b R = 3-phenanthryl   poly(**11b**)

12   R = 1-naphthyl   poly(**12**)   (2)
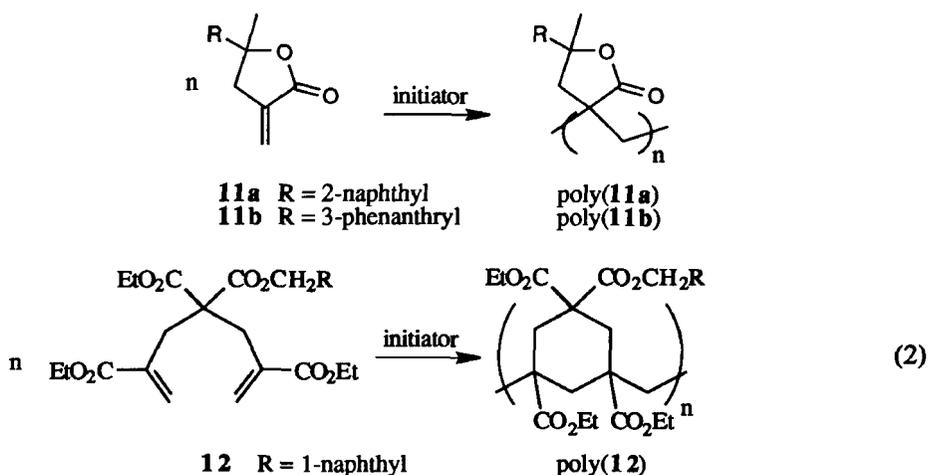
restricted rings on the photophysical properties of these chromophore-bearing polymer chains (14). Poly(**11**) contains five-membered rings perpendicular to the polymer chain, whereas poly(**12**) has six-membered rings in the plane of the polymer chain (assuming exclusive head-to-tail polymerization of component acrylate units). The main chains of these polymers are far less flexible than the less highly substituted polyacrylates studied previously, at least on the timescale of excited state lifetimes, because conformational barriers derived from the rings diminish the importance of competing energy loss pathways, while simultaneously enhancing energy and electron transfer between appended groups.

As expected, the absorption spectra of the monomers and polymers are virtually identical within each series. Fluorescence and singlet energy migration in these chromophore-appended polyacrylates **11** show no excimer formation, although weak excimer emission is observed in **12**, and a strong correlation is observed between the presence of structural defects and the efficiency of excimer emission. Steady-state fluorescence quenching experiments with CCl$_4$ demonstrate that singlet energy migration occurs intramolecularly along these polymer chains.

Conclusions

Surface modification by covalent attachment of surface seeds on which to grow directional polymers or by preformation of rigid polymers that can be covalently attached to a metal or metal oxide surface provide interesting new means for attaining anisotropically oriented absorbers near a metal or metal oxide surface. Conformational rigidity is a key design feature in the preparation of synthetic polymers to be used in such arrays.

Acknowledgments

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