

PHOTOINDUCED ELECTRON TRANSFER IN ORDERED POLYMERS

PROGRESS REPORT

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Guilford Jones, II
Department of Chemistry, Boston University
Boston, Massachusetts 02215

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PHOTOINDUCED ELECTRON TRANSFER IN ORDERED POLYMERS

Long range photoinduced electron transfer between electron donor and acceptor groups is of considerable current interest in terms of strategies for artificial photosynthesis and studies regarding the redox properties of proteins. As part of an extensive study of long range electron transfer involving biopolymers, we have carried out this year investigations of the assembly of electron transfer agents in a system of model short peptides. Also studied is a polyelectrolyte that can adopt a helical conformation when electrostatically complexed with organic dye counter-ions. The principal interest in these systems has to do with the well ordered secondary structures (e.g., the alpha-helices) adopted by peptide polymers, and the capabilities for synthetic modification of peptide side chains and end groups with chromophores or electroactive substituents. The present report gives a brief account of the following elements of work related to photochemical electron transfer themes: (1) the synthesis and photochemical characterization of chromophore-bound peptides and amino acid model compounds based on the amino acids, tryptophan and the spacer residue, alanine (Ala); (2) the study of binding of the cationic organic dye (e.g., styryl-7) to a peptide electrolyte, for which cooperative dye loading and helix formation is important; and (3) completion of the synthesis of a new series of acridinium chromophores that have "rod-like" arrangements of linked aryl rings for assembly of electron donor-acceptor systems that will exhibit especially long lived charge separation.

Peptides and amino acids modified with pyrene chromophores. Modified peptides consisting of the naturally occurring amino acids, L-tryptophan (Trp), and L-alanine (Ala) (Scheme 1) have been prepared. These amino acid derivatives contain a chromophoric group, pyrene sulfonamide (Pyr) covalently bound at the N-terminus, and an electron donor moiety, dimethylphenylenediamine (DMPD) located at the C-terminus (and including other model variations). Photochemical electron transfer (fast kinetics measurements) involving the bound chromophore and the peptide chains is now under investigation through a collaboration with the group of Dr. Michael Wasielewski at Argonne National Laboratory. Picosecond time-resolved absorption measurements have revealed in preliminary work that the forward rate constants for electron transfer between excited pyrene and Trp or DMPD groups occur in

the 10 psec time regime. Significantly, the back electron transfer occurs in the nsec time domain. The latter depends dramatically on the substitution pattern (distance between terminal groups) and provides an example of "inverted region" behavior for a modified biopolymer system. An important problem that is to be resolved in this portion of the project has to do with the role of an aromatic side chain in a Trp moiety in controlling the rate of long distance electron transfer between terminal moieties, Pyr and DMPD. The systematic placement of Trp moieties in tripeptides (e.g., Pyr-Ala-Trp-Ala-DMPD) will provide a unique look at this factor that is of potential importance in the control of rates of charge recombination (separation) in proteins.

Self-assembly in biopolymer - dye complexes. Our studies of polyelectrolytes and their role in the binding of charged organic dyes in water has been extended to the investigation of poly-(L-glutamic acid) (PLGL) which readily binds dyes of the cyanine or merocyanine type. The most novel feature that we have recently discovered for these systems is the tendency of the dye to form dimer aggregates when the chromophore is electrostatically bound, and, remarkably, the tendency of the charged peptide to fold into a helical conformation on interaction with dye counterions (at relatively high loading). In Figures 1-4 below are shown (1) the absorption characteristics of styryl-7 (S7) on binding to PLGL (as dye dimer), (2) the induction of circular dichroism (CD, optical activity) in dye dimers on binding to peptide in two conformational forms whose relative importance depends on pH in a sensitive way, (3) the simultaneous onset of induced CD for bound dye and the adoption of helix conformation as a function of pH, and (4) the "saturation" (adoption of complete helix structure) on loading of sufficient dye counter-ions. Of principal importance in these systems is the ability of peptide-dye complexes to self-assemble into different biopolymer structural motifs that exhibit long range (i.e., one-dimensional, helical) order and arrays of chromophores "stacked" along biopolymer chains. These systems hold particular promise for demonstration of entrainment of charge over nanometer dimensions.

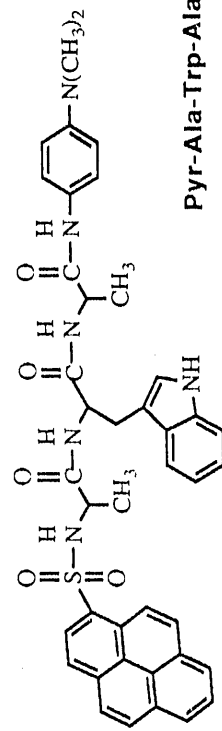
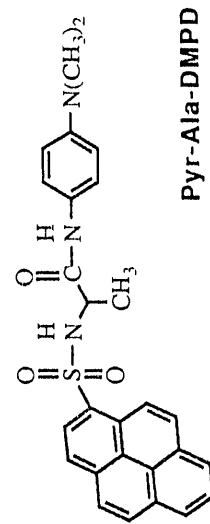
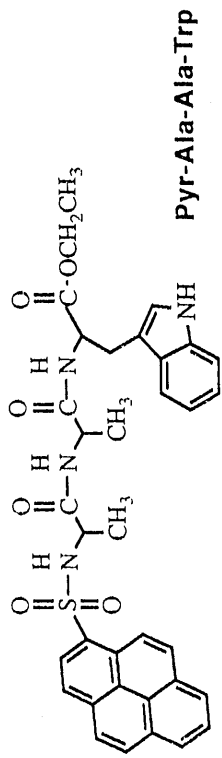
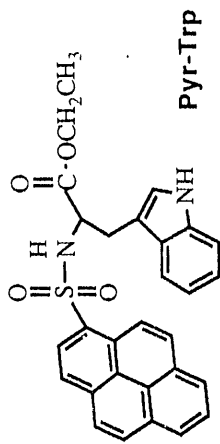
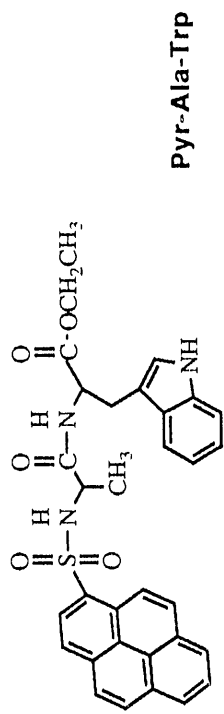
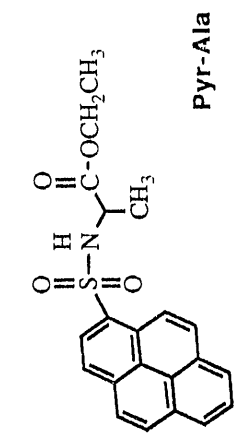
"Twisted" biaryl donor-acceptor structures based on the acridine chromophore. A new series of chromophores constructed from the basic unit of the alkylacridinium species that have rod-like assemblies of linked aromatic rings has been synthesized. These structures, shown in Scheme 2, exhibit the important feature of linkages that have, as their principal geometric variable, rotation

about single bonds that link aromatic rings. These rotations are hindered to an extent that is subtle but predictable, therefore providing a control on the degree of interaction (orbital overlap) between electron donor (aromatic or phenolic) and electron acceptor (acridinium) segments. The expectation is that a systematic adjustment of the length and torsional flexibility of these linkages will provide a means for demonstrating very long lived charge separation, even over relatively short distances (0.5-1.0 nm). Furthermore, these chromophores are designed so that as charged species they can bind to electrolyte biopolymers (e.g., PLGL) or be covalently bound to peptides having other electroactive groups. A series of time resolved emission and absorption measurements has been completed at the Center for Fast Kinetics at the University of Texas at Austin. Radical-pair species have been identified that display lifetimes of a few nanoseconds (as singlet species) or a few microseconds (as triplet species). Further work is underway that would verify that these systems show some of the longest times of charge separation for "short-link" systems that have yet been determined.

RECENT PUBLICATIONS

1. G. Jones, II, C. Oh, and K. Goswami, "The Photochemistry of Triarylmethane Dyes Bound to Polyelectrolytes: Photoinduced Electron Transfer Involving Bound Dye Monomers and Dimers, *J. Photochem. Photobiol. A: Chem.*, **57**, 65 (1991).
2. G. Jones, II and M. Farahat, "Photoinduced Electron Transfer in Flexible Biaryl Donor-acceptor Molecules," *Advances in Electron Transfer Chemistry*, vol 3, P. S. Mariano, Ed., JAI Press, Inc., Greenwich, Connecticut, 1992, in press.
3. G. Jones, II, B. Huang, and S. F. Griffin, "Electron Transfer Photochemistry of Thianthrene. Nucleophile Assisted Photooxidation to Sulfoxide," in preparation.

Scheme 1



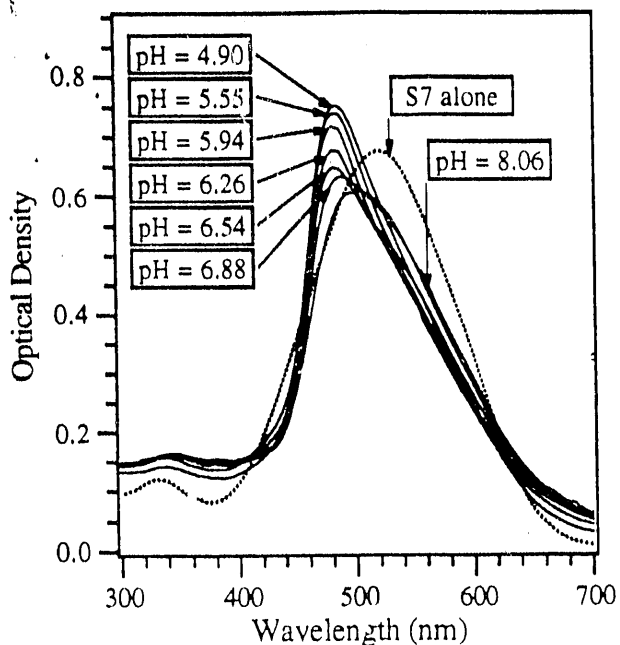


Figure 1 The absorption spectra for 20 μM S7 without and with PLGL (P/D = 2) at various pH.

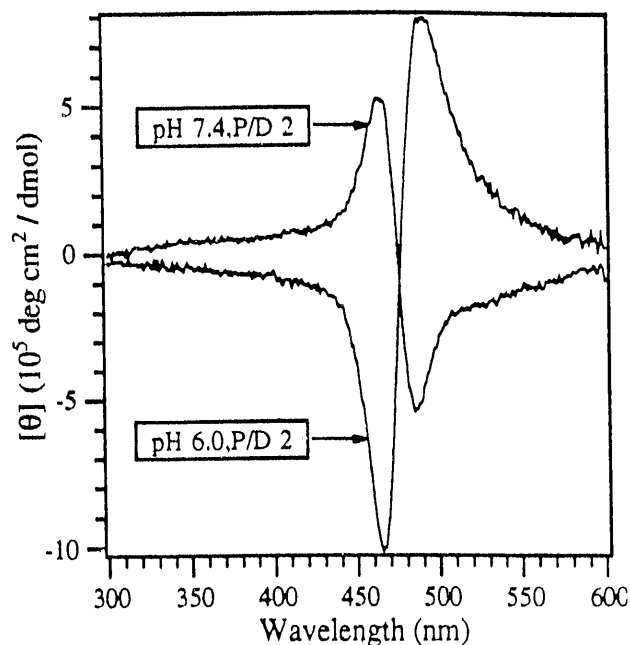


Figure 2 The ICD of S7-PLGL at P/D 2 ([S7] = 20 μM).

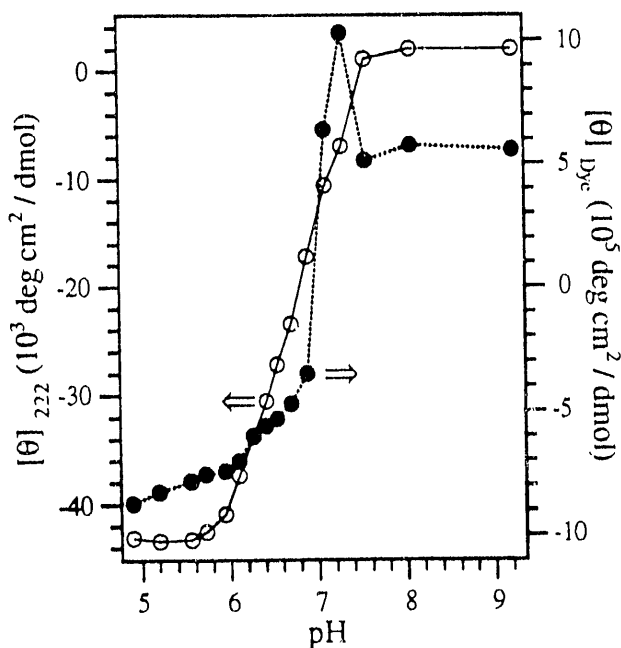


Figure 3 The pH dependence of CD at 222 nm and ICD in the visible region for S7-PLGL (P/D = 2, [S7] = 20 μM). The molar ellipticity of dye is measured at the shorter wavelength extremum of ICD.

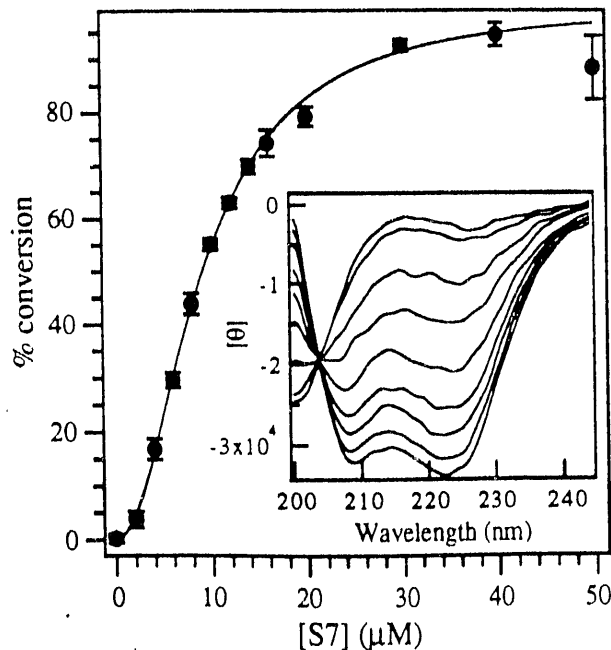
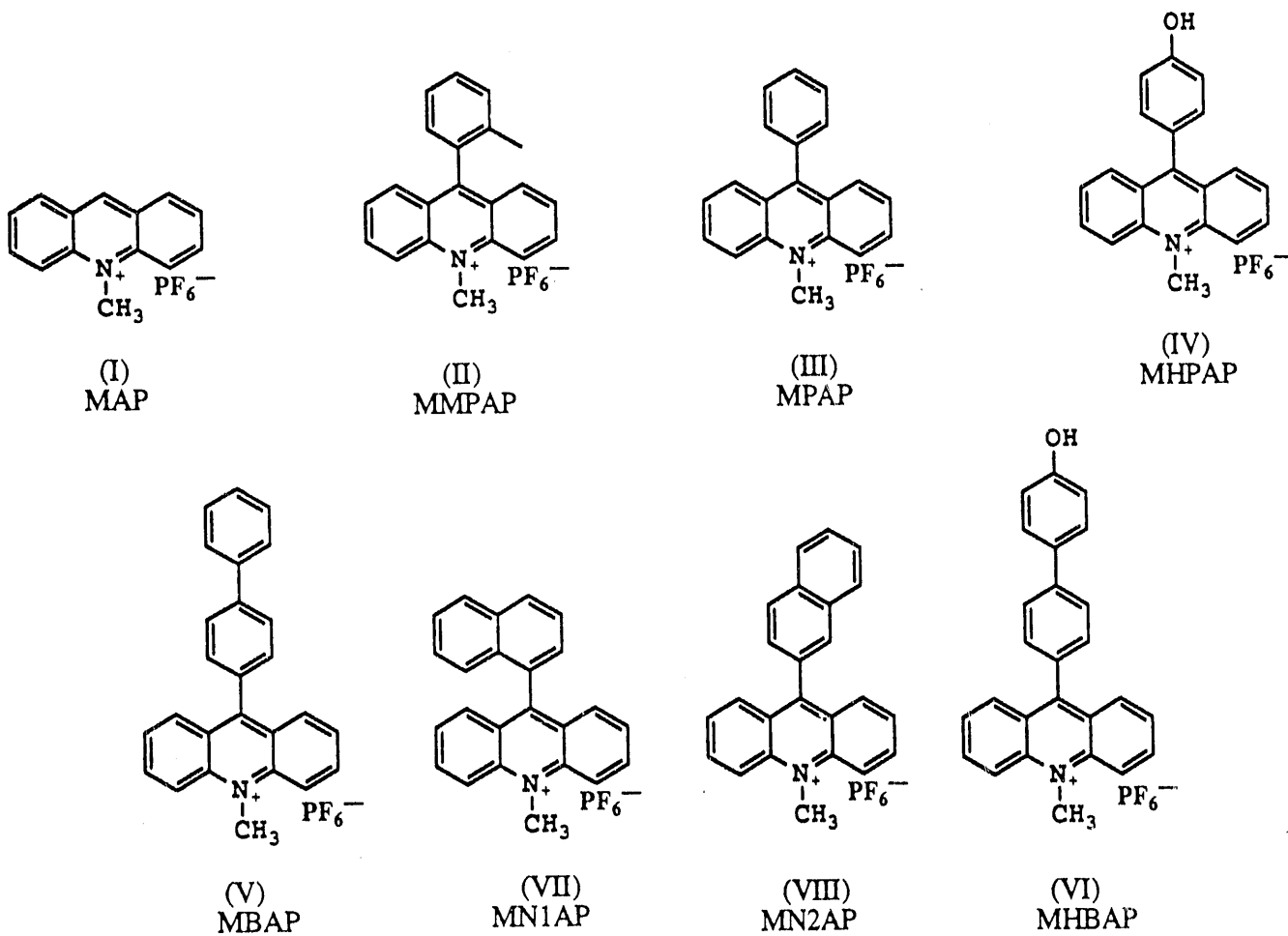


Figure 4 The P/D dependence of uv CD of S7-PLGL (pH 6.1, [PLGL] = 50 μM ; [S7] = 0, 2, 4, 6, 8, 10, 12, 14, 16 μM from top in inset). The percent conversion is calculated as follows:

$$\% \text{ conversion} = \frac{\theta_0 - \theta_{222}}{\theta_0 - \theta_{\infty}}$$

where θ_0 and θ_{∞} are the PLGL ellipticities at zero and infinite [S7] respectively.

Aryl substituted acridinium compounds



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