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The Organic Chemistry of Conducting Polymers

Annual Technical Report

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1. Recent Results.

Results from previous DOE support (a) confirmed a finite confinement width for the soliton, (b) demonstrated the proton-transfer doping of polyacetylene, (c) provided a mechanism for electron-hopping, (d) confirmed the onset of a Peierls distortion in discrete polyenes (i. e., cyanines) (e) established a new class of conductive heteropolymers, and (f) demonstrated the synthesis and covalent attachment of polymerizable "trimers" to a variety of insulating, conductive, and semiconductive surfaces. Many of these results have been summarized in an *Accounts* article.¹ In the last year, we have been able to exploit these results through the synthesis and investigation of a novel set of binuclear complexes which indicate soliton-like communication between the two metal centers. We have also succeeded in synthesizing some new soluble polyheterocycles which demonstrate remarkable conjugation lengths. These materials demonstrate electroluminescence as well, although not yet of sufficient efficiency to issue a press release.

1.1. Intervalence charge-transfer in dinuclear cyanine complexes.

One of our objectives, as well as that of others, is to use a polyene or heteropolymer to connect two nanoelectrodes and examine the existence and the limits for conductivity in a single (unbroken) polymer chain or bundle. At this limit, the distinction between polymer electrochemistry and discrete molecule redox chemistry begins to vanish. A considerable amount of effort in transition metal photochemistry has examined the question of time-dependent charge transport in a dinuclear complex between two metals at different redox states but coupled by some conjugating pathway, e. g., a pyrazine ligand. Curiously, such studies invariably include ligands which require formal reduction or oxidation to achieve electron transport. Similarly, most of the single-strand polymer studies fail to address the problem of "doping", or injecting charge into, a single polymer chain. Since our cyanines may be viewed as a soliton within two pyridinium acceptors, this chemistry provides ready

Figure 1. Charge transport between redox states.

Figure 2. Generation of redox path by deprotonation of DPy7-H dinuclear complex.

entry into a new class of dinuclear complexes containing an intrinsic charge carrier (see Figure 1). Our strategy was as follows: Using a combination of acid/base and redox chemistry, we produced dinuclear (Ru[II]) complexes of our bipyridylpolyene intermediates, using as our starting point the readily available **DPy5**. We prepared the Ru(II)PyCH=CHCH=CHCHPyRu(II) complex by deprotonation of Ru(I)pyCH=CHCH₂CH=CHpyRu(I). The absorption spectrum of this complex was a superposition of the Ru(II) spectrum and the **DPy5** spectrum with some minor spectral shifts. Spectroelectrochemistry of the complex revealed separate waves for oxidation of the Ru(II) and for oxidation of the **DPy5** ligand, with superposition of the spectra for the individual components and no notable shift in the oxidation waves as a function of complexation. Thus there was no evidence for coupling between the two centers, and this approach was abandoned.

Recognizing that what was required for success with the biheteronuclear complexes was a more efficient coupling of metal centers, we have shifted to ferrocene analogs in which the ferrocene would be covalently attached to the solitonic chain. Ferrocene end groups provide stable, low-potential redox active termini and allow strong coupling of the redox centers with the polyene chain. The first two members of this series (**DFc1⁺**, **DFc3⁺**) were generated by literature methods^{2,3}.

The remaining members were synthesized through conventional Wittig methodology. Specifically, a ferrocenyl aldehyde was allowed to react with 1,3-propanebis(triphenylphosphorane) to yield the bisferrocenyl polyene containing a CH₂ group. The polymethine cation was afforded by hydride abstraction with triphenylcarbenium tetrafluoroborate. Precipitation induced by addition of ether in the final step afforded the polymethines as dark green or blue solids that were pure by ¹H NMR spectroscopy. The synthetic pathways leading to **DFc5⁺**, **DFc9⁺** and **DFc13⁺** is shown in Figure 3.

Figure 3. Synthesis of **DFcN⁺**

In Table 1 are presented the absorption maxima of this class of polymethines. These compounds absorb at a much longer wavelengths than the analogous diphenylpolyenyl carbenium ions^{4,5} and carbanions of analogous length.^{5,6} Moreover, the absorption maxima of **DFc3** and **DFc5** are considerably red-shifted relative to the two known isoelectronic bis(cyclopentadienyl)polyenyl anions **DCp3⁻** and **DCp5⁻**,^{5,7} indicating the presence of strong electronic coupling between the electropositive iron complex and the HOMO orbitals of the polyene chain.⁸ However, the incremental shift per vinylene group diminishes with chain length.⁵

A property of linear polyene systems is a reciprocal correlation between chain length and band gap or absorption energy.⁹ When the absorption energies of the diferrocenyl polymethines are plotted vs. $(N_{\text{eff}})^{-1}$, where the N_{eff} is the number of polyene atoms plus 3 per ferrocenyl group (cf. plus 4 for phenyl group), a linear relationship is obtained with an intercept of 0.55 eV (see Figure 4). This intercept, corresponding to the theoretically infinite diferrocenylpolyenyl cation, is close to the absorption maximum of 0.6-0.8 eV for p-doped polyacetylene¹⁰ in which an odd-alternant hydrocarbon cation, a soliton, is the presumed absorptive species. This confirms that the strongly allowed transition is $\pi \rightarrow \pi^*$ with extensive delocalization into the ferrocenyl moieties which vanishes at longer chain lengths.

Figure 4. Plot of ΔE vs. $1/N$.

To what extent does the presence of a polymethine cation affect the electrochemical communication between the two ferrocenyl centers? Bisferrocenyl complexes coupled with a variety of carbon chains have been investigated, but in no case has measurable separation between the first and second oxidation waves been reported for spacers longer than two atoms.¹¹ The DFcN cations show separable oxidation potentials with up to 13 carbon atoms between metal centers (see Table 2). Thus the interposition of a solitonic moiety between the two metal centers has a dramatic effect on both electronic and electrochemical coupling between the two ferrocenes. The time scale of the electrochemical measurement does not allow us to determine whether the peak separation represents a dynamic effect involving formation of one ferrocinium followed by cation ("soliton") migration to distort the other end, or a static effect involving a true mixed valence state. Such studies require time-resolved spectroscopic analysis of the half-oxidized species and are now in progress. Nevertheless, these results provide impetus for the use of odd-alternant polymethine cations as molecular wires in the molecular architecture of electroactive systems. This work has been accepted for publication in *J. Am. Chem. Soc.*

Table 1. Absorption maxima of polymethines $X(CH)_nX^{+/-}$ (λ , nm).

n =	1	3	5	7	9	11	13	17
DPN ⁺ (X=Ph) ^a	--	498	554	610	660	714	758	
DPN ⁻ (X=Ph) ^b	453	557	571	641	695	751	800	900
DCpN ⁻ (X=C ₅ H ₅) ^c	--	564	665	--	--	--	--	
DFcN ⁺ (X=C ₅ H ₅) ^d	618	781	892	--	1067	--	1187	

Table 2: Half-wave redox potentials for bis(ferrocenyl)polymethine cations DFcN⁺^a

	DFc1	DFc3	DFc5	DFc9	DFc13
E _{1/2} (1) ^b	0.39	0.42	0.37	0.36	0.34
E _{1/2} (2) ^c	0.72	0.60	0.51	0.43	0.38
ΔE	0.33	0.18	0.14	0.07	0.04

1.2. Heteropolymers.

1.2.1. 3-Alkylbithiophenes. We have been interested in the production of soluble, structurally homogeneous polyheterocycles containing a variety of functional groups for nanoscale applications. Our approach has been to use triheterocyclic "monomers" to reduce the oxidation potential and the produced more regiospecific polymers.¹² We have now achieved the synthesis of poly-(3-undecanylthienyl-co-thiophene) (**pTTC₁₁**) using as our monomer a bithiophene containing an alkyl group at C-3. Use of this "inside" alkyl monomer avoids the possibility that direct head-to-head coupling would lead to steric interference. Moreover, preliminary analysis indicates that the polymer is not formed in a random fashion, but that some self-assembly may contribute to a polymer with largely head-to-tail coupling. Finally, consideration of the extraordinarily long wavelength absorption indicates a high degree of order and long-range planarity.

The synthesis of the monomer is shown in Scheme I. It can be prepared conveniently by a "one-pot" procedure, starting with Pd(dppf)Cl₂-mediated coupling of 2,3-dibromothiophene with 2-bromomagnesium thiophene. The resulting 3-bromo-2,2'-bithiophene is treated with undecylmagnesium bromide using Ni(dppp)Cl₂ catalysis to yield 3-undecyl-2,2'-bithiophene in overall 75% yield (see Figure 5)

Figure 5. Synthesis of 3-undecyl-2,2'-bithiophene.

Chemical polymerization was carried out in nitrobenzene solution, using a 4-fold excess of FeCl_3 as an oxidant, at room temperature over 4 days. The polymeric material was precipitated from methanol, filtered and fractionated by continuous extraction with methanol, followed in turn by acetone (fraction 1), methylene chloride (fraction 2) and tetrahydrofuran (fraction 3). The THF soluble fraction exhibited the longest absorption wavelength known for a polythiophene, indicating the presence of a high conjugation length (see Table 3).

Table 3.

Polymer Fraction	λ_{max} (a) -solid (b) -solution in CHCl_3	$\overline{M}_w^*$	$\overline{M}_n^*$	Polydispersity Index $\overline{M}_w / \overline{M}_n$
1 (acetone soluble)	(a) 451.0 (b) 429.0	13614	11774	1.16
2 (CH_2Cl_2 soluble)	(a) 512.0 (b) 456.5	11209	10194	1.10
3 (THF soluble)	(a) 539 (b) -	22152	15012	1.47

*Molecular weight distribution averages (area normalization) [w(t)] GPC analysis performed on Waters system 510 pump, phenogel column 300mm length, $\overline{M}_w$ range 5,000 - 1,000,000. solvent: THF, UVVis detector at $\lambda=450\text{nm}$.

1.2.2. *Poly(thiophene-3-alkanephosphonates}*. We have synthesized diethyl thiophene-3-undecanephosphonate and have discovered that its polymer is remarkably solvatochromic and thermochromic, undergoing a transition from yellow to purple as the temperature is increased or upon dissolution in a hydrogen bonding solvent. This phenomenon is being investigated further.

1.2.3. *Rod polymers.* The requirement for ordered, liquid-crystalline-like monomers which can be electropolymerized at the atomic level suggests that simple polythiophenes or pyrroles, which do not form ordered, layered materials, may not be the best candidates for nanolithography. Rather, monomers which possess translational symmetry are required. In addition to the "even" oligomers of the type shown above, rod polymers are also attractive. A suitable alternative is a [a,d]bisthienobenzene. Although the monomer is known¹³ and has been electropolymerized, little is known about its morphology. We have reproduced synthetic details provided by Pomerantz on derivatives.¹⁴ We have also synthesized analogs containing 7,8-bis(alkoxymethyl) derivatives, which electropolymerize easily to form soluble materials (see Figure 6).

Figure 6. Synthesis of alkoxyated benzodithiophene.

2. Proposed work.

2.1. **Bi- and poly-nuclear complexes.** The bis(ferrocene) complexes and their analogs provide the first opportunity for actually measuring the rates of soliton propagation down a polyene chain. Our strategy is as follows: We will differentiate the two ends of a binuclear complex either by changing the metal at one end, e. g., ruthenocene, or by modifying the ligand to a pentamethyl derivative. The latter approach has the added benefit of increasing solubility. This will allow us to selectively oxidize one end and photochemically promote an electron from the other end into the solitonic (conduction) band. Time resolved analysis of the spectral evolution will allow us to determine the rate of soliton migration. In this regard, the recently acquired femtosecond laser system, in collaboration with Professor Mostafa El-Sayed, will loom very important.

In a related project, we will "string together" polymers and oligomers consisting of solitonic chains between ferrocene centers. Such polymers will allow solitonic

conduction of redox states between ferrocenes and "hopping" of electrons from one metal to the next. There is the possibility of viewing such systems as true molecular neural networks, although any applications of this technology at this point are purely speculative.

2.2. Heteropolymers. We will continue our investigation in applications of our soluble conductive films. Prof. A. S. Abhiraman, in the School of Textile and Fiber Engineering, is in the process of spinning fibers and films from our materials to determine if they can be incorporated into commercial fibers. There is a great deal of interest in conductive fibers for antistatic applications in the textile industry. In the meantime, we will continue our development of new soluble polymers and an understanding of their electrochemistry.

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4. Active Grants.

National Science Foundation, "Charge Distribution in Photoexcited Molecules," CHE-9111768, 1-1-91 to 6-30-97, including automatic six-month extension \$588,000.

National Aeronautics and Space Administration, "High-Performance Polymer and Ceramics Center", consortium with Clark Atlanta University, 1-1-92 to 9-30-96. total budget ca. \$8.5M, value to L. M. T. \$80-100,000.

Department of Energy, "The Organic Chemistry of Conducting Polymers," DE-FG05-85ER45194, 7-1-91 to 12-31-97, \$480,000.

National Science Foundation, "Laser Spectroscopy Instrumentation," 8-1-95 to 7-31-96 (Major instrumentation grant), \$400,000.

5. Publications (93-95. DOE acknowledgment marked by *.

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6. Personnel

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Michael Terapane, Ph. D. student. (B. S., Virginia Institute of Technology and S. U.)

Budget information removed