Bis(ferrocenyl)polymethine Cations. A Prototype Molecular Wire with Redox-Active End Groups

Laren M. Tolbert,* Xiaodong Zhao, Youzhen Ding, and Lawrence A. Bottomley

School of Chemistry and Biochemistry
Georgia Institute of Technology
Atlanta, Georgia 30332-0400

Received September 18, 1995

The concept of a "molecular wire", i.e., a conductive path of atomic orbitals allowing long-range intramolecular electron or hole transfer, has been a tantalizing dream since the early theoretical work of Aviram and Ratner.[1] The most common type of molecular wire involves a symmetrical polyene containing acceptor moieties at the polyene termini. Reduction of one acceptor introduces the charge carrier,[2,3] which migrates through the polyene chain to the other terminus. A recent modification of electroactive polyenes involves mixed-valence binuclear complexes bridged by polyenes, in which intervalence transfer facilitates the long-range electron transfer.[4] Since doped polyacetylene, the conductive polymer equivalent to these polyenic systems, exhibits conduction via odd-alternant hydrocarbon segments called "solitons", we concluded that more effective communication between redox-active end groups could be achieved with an odd-alternant polyenyl, i.e., polymethine, ion DXN* (see Figure 1).[5] The nonbonding molecular orbital characteristic of such systems could provide a low-energy pathway for the carrier electron, in contrast to the high-energy antibonding orbital in even-alternant polyenes.[6,7] We have previously provided evidence for solitonic behavior in polymethines using α,ω-diphenylpolyenyl anions (DPN^-, X = Ph)[8] and α,ω-dipyridocyanines ($DPyN^+$, X = py-CH_3).[9] We now extend this approach to molecular wires involving polymethines with redox-active end groups. In this communication, we report the synthesis and characterization of α,ω-bis(ferrocenyl)polymethine cations (acronym $DFcN^+$, X = C_5H_5) as part of our systematic investigation of solitonic behavior in molecules ("solitons in a box").[10] 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 according to literature methods.[11,12] 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 bis(ferrocenyl)polyene containing a CH_2 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 pathway leading to $DFc5^+$, $DFc9^+$and $DFc13^+$, is shown in Figure 2.

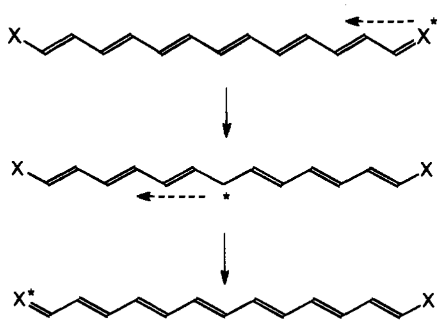

Figure 1. Electron or hole exchange through soliton migration (* = − or +).

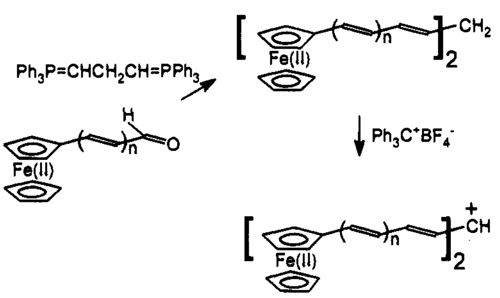

Figure 2. Synthesis of $DFcN^+$.

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_5H_5)[c]		564	665					
$DFcN^+$ (X = C_5H_5)[d]	618	781	892		1067		1187	

[a] References 13, 14. [b] Reference 8a. [c] Reference 15. [d] This work.

In Table 1 are presented the absorption maxima of this class of polymethines. These compounds absorb at much longer wavelengths than the analogous diphenyl(polyenyl)carbenium ions[13,14] and carbanions of analogous length.[8,10a,14] Moreover, the absorption maxima of DFc3 and DFc5 are considerably red-shifted relative to those of the two known isoelectronic bis(cyclopentadienyl)polyenyl anions $DCp3^-$ and $DCp5^-$,[14,15] indicating the presence of strong electronic coupling between the electropositive iron complex and the highest occupied molecular orbitals of the polyene chain.[16] However, the incremental shift per vinylene group diminishes with chain length.[14]

---

(1) Aviram, A.; Ratner, M. A. *Chem. Phys. Lett.* **1974**, *29*, 277.

(2) Arrhenius, T. S.; Blanchard-Desce, M.; Dvolaitzky, M.; Lehn, J.-M.; Matthete, J. *Proc. Natl. Acad. Sci. U.S.A.*, **1986**, *83*, 5355.

(3) Lehn, J.-M. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1304.

(4) (a) Bonvoisin, J.; Launay, J.-P.; Rovira, C.; Veciana, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2106. (b) Ribou, A. C.; Launay, J. P.; Takahashi, K.; Nihira, T.; Tarutani, S.; Spangler, C. W. *Inorg. Chem.* **1994**, *33*, 1325. (c) Woitellier, S.; Launay, J.-P.; Spangler, C. W. *Inorg. Chem.* **1989**, *28*, 758. (d) Launay, J.-P. In *Mixed Valency Systems: Applications in Chemistry, Physics and Biology*; Prassides, K., Ed.; Kluwer Academic Publishers: Dordrecht, 1991; p 321.

(5) The relationship between conductivity and odd vs even disposition has been pointed out elsewhere: (a) Reimers, J. R.; Hush, N. S. *Chem. Phys.* **1990**, *146*, 89. (b) Joachim, C.; Launay, J. P.; Weitellier, S. *Chem. Phys.* **1990**, *147*, 131.

(6) André, J.-M.; Delhalle, J.; Brédas, J.-L. *Quantum Chemistry Aided Design of Organic Polymers*; World Scientific Publishing: Teaneck, NJ, 1991.

(7) Reimers, J. R.; Hush, N. S. *Chem. Phys.* **1990**, *146*, 89.

(8) (a) Tolbert, L. M.; Ogle, M. E. *Mol. Cryst. Liq. Cryst.* **1990**, *189*, 279. (b) Tolbert, L. M.; Ogle, M. E. *J. Am. Chem. Soc.* **1990**, *112*, 9519. (c) Tolbert, L. M.; Ogle, M. E. *J. Am. Chem. Soc.* **1989**, *111*, 5958.

(9) Tolbert, L. M.; Zhao, X. *Synth. Met.*, **1993**, *55–57*, 4788.

(10) Tolbert, L. M. *Acc. Chem. Res.* **1992**, *25*, 561.

(11) (a) Jutz, C. *Tetrahedron Lett.* **1959**, 1. (b) Boev, V. I.; Dombrovskii, A. V. *Zh. Obshch. Khim.* **1980**, *50*, 2520.

(12) (a) Nesmeyanov, A. N.; Postnov, V. N.; Sazonova, V. A.; Galakhova, T. N.; Kuznetsov, A. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, 2172–2175. (b) Boev, V. I.; Dombrovskii, A. V. *Zh. Obshch. Khim.* **1985**, *55*, 1173.

(13) Dähne, S.; Radeglia, R. *Tetrahedron* **1971**, *27*, 3673.

(14) Fabian, J.; Zahradnik, R. *Wiss. Z. Tech. Univ., Dresden* **1977**, *26*, 315.

(15) Dörr, F.; Kotschy, J.; Kausen, H. *Ber. Bunsenges. Phys. Chem.* **1965**, *69*, 11.

(16) For a system based upon metal–carbene end groups, see: Spotts, J. M.; Marder, S. R. *Adv. Mater.*, **1992**, *4*, 100.

(17) (a) Brédas, J. L.; Silbey, R.; Boudreaux, D. S.; Chance, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 6555. For early work on cyanines, see: (b) Kuhn, H. *J. Chem. Phys.* **1949**, *17*, 1198. (c) Kuhn, H. *Chimia* **1955**, *9*, 237. (d) Kuhn, H. *Angew. Chem.* **1959**, *71*, 93.

0002-7863/95/1517-12891$09.00/0

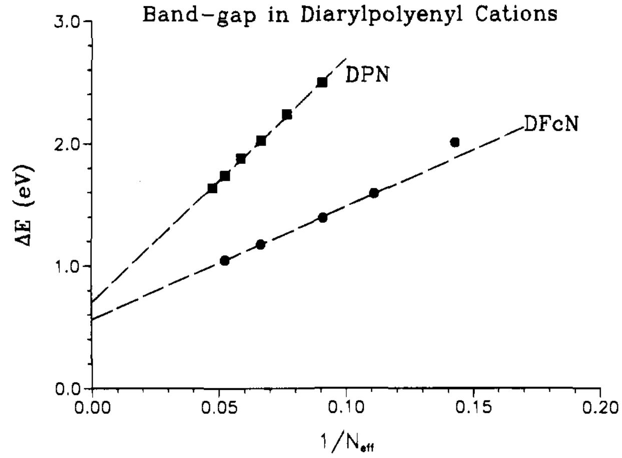

Figure 3. Plot of ΔE vs $1/N$.

A property of linear polyene systems is a reciprocal correlation between chain length and band gap or absorption energy.[17] When the absorption energies of the bis(ferrocenyl)polymethines are plotted versus $(N_{\mathrm{eff}})^{-1}$, 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 (Figure 3). This intercept, corresponding to the theoretically infinite bis(ferrocenyl)polyenyl cation, is close to the absorption maximum of 0.6–0.8 eV for p-doped polyacetylene,[18] 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.

To what extent does the presence of a polymethine cation affect the electrochemical communication between the two ferrocenyl centers? Bis(ferrocenyl) 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.[19] Spangler and co-workers have synthesized analogues with up to six double bonds which retain electrochemical peak separation.[20] However, the *trans*-stilbene analog, bis(ferrocenyl)ethylene, shows only a 120 mV separation between the first and second oxidation waves.[19a] In any event, 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.

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

[a] V vs SCE, midpoint of oxidation and reduction waves (in CH_2Cl_2/$LiClO_4$). [b] First half-wave (oxidation) potential. [c] Second half-wave (oxidation) potential.

Acknowledgment. Support of this research by the U.S. Department of Energy through Grant No. DE-FG05-91ER45194 is gratefully acknowledged.

JA953197H

---

(18) Suzuki, N.; Ozaki, M.; Etemad, S.; Heeger, A. J. MacDiarmid, A. G. *Phys. Rev. Lett.* **1980**, *45*, 1209; erratum, 1483.

(19) (a) Floris, B.; Tagliatesta, P. *J. Chem. Res.* **1993**, 42. (b) Gladysz has shown that polyyne chains directly connected to metal centers can exhibit electrochemical communication over eight carbons or even longer: Brady, M.; Weng, W.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1994**, 2655. See also: (c) Bartik, T.; Bartik, B.; Brady, M.; Dembinski, R.; Gladysz, J. A. *J. Am. Chem. Soc.*, submitted. (d) Le Nurvor, N.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1992**, 357.

(20) Ribou, A.-C.; Launay, J. P.; Sachtleben, M. L.; Li, H.; Spangler, C. W. To be submitted.