a rate constant of 1.9×10^7 M^{-1} s^{-1} at 291 K. This rate for the solution-phase reaction, which is only $\sim 10^{-3}$ of the encounter rate, may be spin-restricted, but in any case, it suggests that the assumption[3b] of a collision-controlled rate for the gas-phase **1** + O$_2$ reaction may be in error by a similar factor. If so, the corrected rate for the gas-phase reaction in turn would require revision of the derived[3b] heat of formation of **1**.

Attempts to quench the flash photolytically produced 490-nm transient with conventional dienophiles (diethyl fumarate, maleic anhydride, fumaronitrile) were unsuccessful. This places an upper limit of $\sim 10^4$ M^{-1} s^{-1} for the reaction rate of **1** with these traps. This slow rate of reaction with alkenes is not surprising; frontier MO considerations predict that **1** should be less reactive toward electron-poor dienophiles than the electron-rich biradicals 3,4-dimethylenefuran and 3,4-dimethylenethiophene, which are quenched by such reagents under flash photolytic conditions.[4a,b]

The factor of $\geq 10^6$ by which the dimerization rate of **1** exceeds that[9] of the closed-shell molecule *o*-quinodimethane is a dramatic consequence of non-Kekulé character in **1**. Dimerization rates in the 10^{10} s^{-1} range are not expected for the hypothetical alternative bicyclic structure **3**. The hypothesis that photolysis of **2** gives rise mainly (95%) to the bicyclic hydrocarbon **3** and a small amount (5%) of **1**, previously discounted[2] on other grounds, is also refuted by the absolute rates observed here, since the rate constant deduced from a hypothetical 20-fold increased extinction coefficient for **1** would have to be 400 times the encounter-limited maximum rate.

The absolute rate measurements thus help to exclude **3** and confirm the previous assignment[2] of biradical **1** as the carrier of the observed CP MAS ^{13}C NMR and UV–vis spectra. Our present and previous[2] findings are consistent with the theoretical predictions[10] of a singlet state for this disjoint species.

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Thiophene–Silole Cooligomers and Copolymers

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Polythiophenes, as well as other π-conjugated polymers, have received considerable attention in research on conducting polymers and molecular electronics.[1] Current interest has especially been directed toward structure modifications, including side chain introduction for solubility improvement[2] and for development of new functions,[3] control of the chain lengths,[4] regularity,[5] and
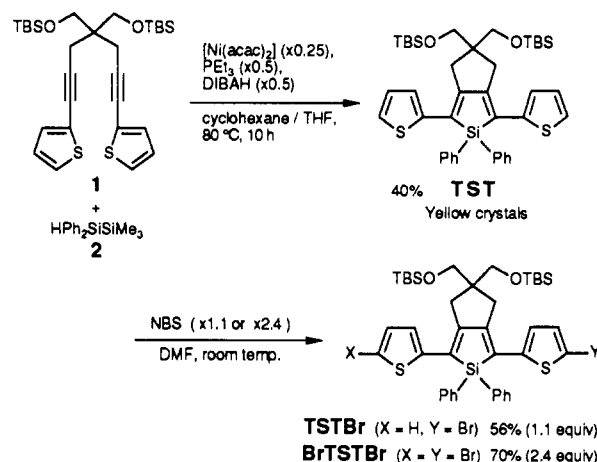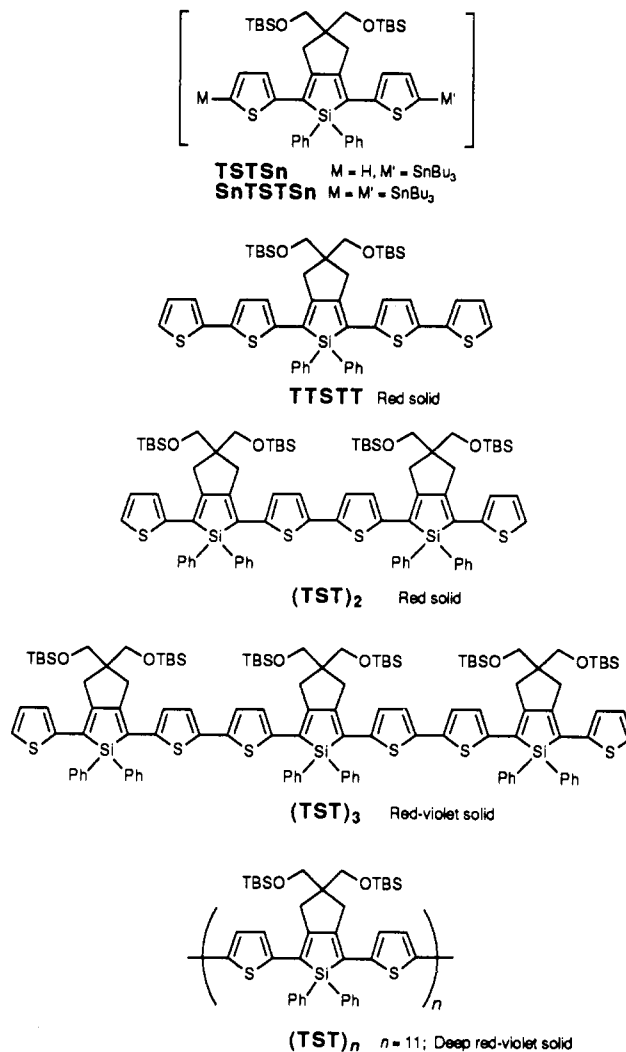
Scheme I

Chart I

geometry,[6] and the synthesis of copolymers and cooligomers with other conjugated ring systems in the main chain.[7]

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Communications to the Editor

Table I. UV–Visible Spectral Data for Thiophene–Silole Cooligomers and Copolymers and Thiophene Homooligomers and Homopolymers[a]

| compound | no. of thiophene and silole, T_nS_m | UV–vis absorptions | | reference |
		λ_{max} (nm)	log ϵ	
TST	T_2S	267	3.88	this work
		416	4.27	
TTSTT	T_4S	473	4.64	this work
(TST)$_2$	T_4S_2	505	4.86	this work
(TST)$_3$	T_6S_3	549	4.96	this work
(TST)$_n$ ($n \approx 11$)	$T_{22}S_{11}$	594	4.52[b]	this work
		615	4.51[b]	
terthiophene	T_3	353[c]		d
quaterthiophene	T_4	391[c]		d
quinquethiophene	T_5	418[c]		d
T11 d3(2,6,10)[e]	T_{11}	462		5b
P3HT[f]	T_{300}[g]	435[h]		2c

[a] In chloroform, unless otherwise stated. [b] Per TST monomer unit. [c] In benzene. [d] Sease, J. W.; Zechmeister, L. *J. Am. Chem. Soc.* **1947**, *69*, 270 and 273. [e] Undecithiophene with three dodecyl groups at thiophene units 2, 6, and 10. [f] Poly(3-hexylthiophene). [g] Based on $M_w \approx 48\,000$. [h] in THF.

Reported herein are the first syntheses and properties of thiophene–silole (silacyclopentadiene) cooligomers and copolymers.[8,9] We anticipated that the introduction of the electron-deficient (electron-accepting) silole rings[10] into the electron-excessive polythiophene chain would lead to considerable perturbation in the π-electron system, such as intramolecular charge transfer.[11] Now we present a synthesis of thiophene–silole copolymers consisting of a thiophene–silole–thiophene (TST) skeleton as a monomer unit; hereafter thiophene and silole are abbreviated to T and S, respectively. The TST monomer (yellow crystals) was prepared by the nickel-catalyzed intramolecular cyclization[12] of the thiophene-containing 1,6-diyne **1**[13] with hydrodisilane **2** in moderate yields, as shown in Scheme I. Selective mono- and dibromination with NBS in DMF[15] of TST afforded

TSTBr and BrTSTBr, respectively (Scheme I).

Cooligomers and copolymers prepared in this study, together with the requisite organometallic reagents, are listed in Chart I. A variety of conditions have been examined for the synthesis of the five-ring system TTSTT by nickel- or palladium-catalyzed cross-coupling of BrTSTBr with 2-thienyl organometallics such as zinc,[16] boronic acid,[17] and tin[17a,18] reagents. While the zinc method formed a mixture of oligomers arising from a halogen/metal exchange, the boron and tin methods afforded TTSTT (red crystals) in 85% and 63% yields, respectively. The dimer (TST)$_2$ (red solid) was obtained in 75% yield in one pot by a palladium-catalyzed cross-coupling reaction[18] of TSTBr with TSTSn generated from TSTBr by successive treatment with *n*-BuLi and *n*-Bu$_3$SnCl. The trimer (TST)$_3$ (red violet solid) and the polymer (TST)$_n$ (deep red violet solid) were synthesized by similar palladium-catalyzed cross-coupling reactions[18] of SnTSTSn, prepared from TST via metalation with *n*-BuLi/TMEDA followed by treatment with *n*-Bu$_3$SnCl, with 2 equiv of TSTBr, and with BrTSTBr, respectively, in 58% and 65–77% yields. Even the trimer is soluble in common organic solvents including hydrocarbons due to the aliphatic side chains on the silole rings. The polymer (TST)$_n$ ($M_w = 12\,600$, $M_n = 7700$, $M_w/M_n = 1.64$, $n \approx 11$) is slightly soluble in CHCl$_3$, giving a deep blue solution. All of the cooligomers and polymer are air stable.

The structure of TST monomer has been determined by X-ray crystallography, which demonstrates the highly planar arrangement of the three rings; there are small twists between the outer thiophene rings and the central silole ring: 10.21° and 7.04°.

The UV–visual absorption data, summarized in Table I, indicate that the thiophene–silole combination causes large red shifts compared with the thiophene homooligomers and homopolymers. Thus, the cooligomers TST (416 nm) and TTSTT (473 nm) display about 60-nm red shifts compared with the same three and five thiophene ring systems T_3 (353 nm) and T_5 (418 nm), respectively. Remarkably, the absorption maximum of the silole-containing six-ring system (TST)$_2$ (505 nm) exceeds those of the homooligomers having 11 thiophene units and of polythiophenes. Of particular interest are the broad absorptions of the copolymer (TST)$_n$ at 594 and 615 nm, which are the longest wavelengths ever found for thiophene-based polymers in the neutral undoped state.[19] These unusual optical properties strongly suggest the occurrence of intramolecular charge transfer from thiophene ring to silole ring as mentioned above.

While the bulk conductivity of a compressed pellet prepared from the powdery polymer (TST)$_n$ was $<1 \times 10^{-11}$ S cm^{-1}, doping with I$_2$ vapor (about 120 wt %) raised the value to 10^{-3} S cm^{-1}, as measured by using a four-probe technique in vacuo at room temperature.

Further studies on the promising thiophene–silole cooligomers and copolymers are currently under way in our laboratories for improvement of the conductivity by achieving higher molecular weights and/or by changing the T/S ratios and for measurements of other physical properties.

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ment of the UV–vis spectra and the molecular weights.

Supplementary Material Available: Experimental procedures for the synthesis of TST, TSTBr, BrTSTBr, TTSTT, (TST)$_2$, (TST)$_3$, and (TST)$_n$, listings of their spectral and analytical data, and details of the X-ray structure, crystal data, atomic coordinates, thermal parameters, and full data of bond distances and angles for TST (10 pages). Ordering information is given on any current masthead page.

Structural Characterization of the Binuclear Mn Site in *Lactobacillus plantarum* Manganese Catalase

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There is presently substantial interest in multinuclear Mn proteins. In addition to the photosynthetic oxygen evolving complex (OEC), which contains four Mn atoms,[1] Mn clusters have been found in several non-heme catalases[2-4] and in ribonucleotide reductase.[5] Mn catalases[2-4] contain a binuclear Mn site and have at least four accessible oxidation states.[6-9] We report here the results of an EXAFS study of the reduced, Mn(II)/Mn(II), and the superoxidized, Mn(III)/Mn(IV), derivatives of the *Lactobacillus plantarum* Mn catalase.

Mn catalase is inactivated by treatment with NH$_2$OH + H$_2$O$_2$,[6a] giving a superoxidized species having a 16-line EPR signal.[7,9] The temperature dependence and the hyperfine coupling constants[10] are consistent with a strongly coupled Mn(III)/Mn(IV) dimer, and X-ray edge spectra confirm this assignment.[9] Unfortunately, these give no direct information regarding the Mn–Mn separation. EPR spectroscopy shows that the Mn ions in reduced catalase are weakly coupled,[7] but again provides no information on the Mn–Mn distance. Preliminary crystallographic results[4,11] suggest an Mn–Mn distance of ca. 3.6 Å, although the oxidation state was not given. Knowledge of the Mn–Mn distances could be used to define the Mn-bridging ligands,[12] since (μ-O)$_2$ structures
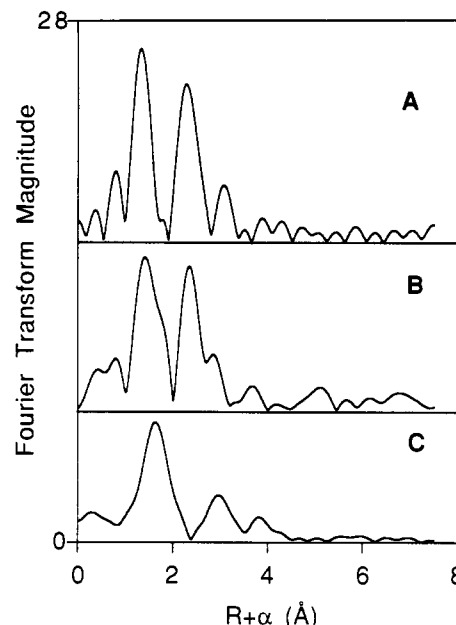

Figure 1. Fourier transforms (k^3 weighted, $k = 3.5$–11.8 Å^{-1}) of the EXAFS spectra for (A) S$_1$ state of the OEC, (B) superoxidized catalase, and (C) reduced catalase. Spectra offset vertically for clarity. OEC data from ref 14b.

Table I. Manganese Catalase EXAFS Fitting Results[a]

	superoxidized			reduced			Mn(II)-(imidazole)$_6$[b]
	N	*R* (Å)	$\Delta\sigma^2 \times 10^3$	*N*	*R* (Å)	$\Delta\sigma^2 \times 10^3$	*R* (Å)
O	2	1.82	2.1				
N/O	4	2.14	-1.9	6	2.19	0.0	2.27
Mn	1	2.67	1.4				
C	4	3.00[c]	0.0	8	3.16	6.9	3.27
N/C	4	4.33[c]	-0.8	4	4.42	-1.9	4.43

[a] Best fit to unfiltered data. Coordination numbers were fixed at integer values giving the best fits. Debye–Waller factors (σ^2) given as Å$^2 \times 10^3$. Absolute σ^2 is reported for Mn–Mn; other values are $\Delta\sigma^2$ relative to reference compound. [b] Crystallographic data from ref 19. [c] Shell is poorly defined. An alternate minima exist at 3.3 Å (C) and 3.9 Å (N/C).

have Mn–Mn ≈ 2.7 Å, (μ-O)(μ-OH) structures have Mn–Mn ≈ 2.8 Å,[13] (μ-O)(μ-carboxylato)$_2$ structures have Mn–Mn ≈ 3.0–3.3 Å,[12] and other geometries (e.g., hydroxo and carboxylato or only carboxylato bridges) have longer, weaker Mn–Mn interactions that may not be detected with EXAFS.

Catalase was isolated as described previously.[9] X-ray absorption spectra were measured and analyzed using conventional methods.[14,15] The Fourier transform for superoxidized catalase (Figure 1B) has two principal peaks at $R + \alpha \approx 1.4$ and 2.3 Å, corresponding to Mn–(O,N) nearest neighbor and Mn–Mn scattering, respectively. Perhaps the most striking feature of this spectrum is its similarity to the Fourier transform for the OEC[14,17] (Figure

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