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Influence of π-Stacking on the Redox Properties of Oligothiophenes: (α-Alkyloligo-thienyl)para[2.2]cyclophanes

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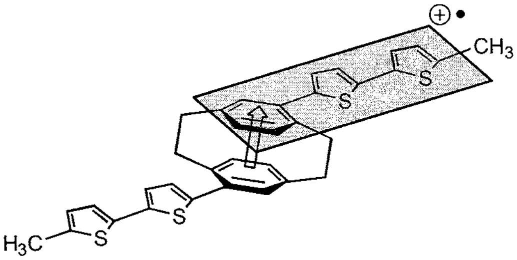
ABSTRACT



Oligothienyl-substituted paracyclophanes bearing α-thienyl substituents, which block polymerization at these sites, undergo oxidation to form stable radical cations and dications. Splitting of the first voltammetric oxidation wave of stacked dimers into two single-electron processes corresponding to formation of the stacked mono(radical cation) and the stacked bis(radical cation) illustrates the influence of π-stacking on the behavior of conjugated chains, which serve as models for stacked polarons in conjugated polymers.

The conductivity of doped conjugated organic polymers requires migration of delocalized carriers (solitons, polarons, bipolarons) along conjugated chains and through π-stacks.[1] However, most physical−organic studies of this process make use of linear polyenes as one-dimensional models, which are used only to probe the delocalization and migration of carriers along individual noninteracting chains.[2] The effect of stacking model charge carriers has been addressed by the covalent linkage of conjugated oligomers[3] and by assembly of π-dimers of ion radicals in solution.[4]

The through-space electronic interaction between neutral and charged stacked arenes has previously been studied by examination of substituent effects,[5] spectroscopy,[6,7] and electrochemistry[8,9] of cyclophanes in which the stacking interaction is fixed through covalent bonds. The effect of stacking on delocalized excitons of *neutral* chromophore-substituted cyclophanes has been addressed extensively by Bazan.[10] We have undertaken a study of *cationic* (i.e., p-doped) oligothiophene-substituted [2.2]paracyclophanes in an attempt to introduce a second dimension to models of delocalized charge carriers in conjugated, conducting, polymers. Previous reports show that bis(2-thienyl)-cyclophane, **CP−Th$_2$**,[11] along with the bis(dithienyl)[12] analogue, is subject to electrooxidative polymerization through the un-

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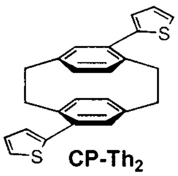
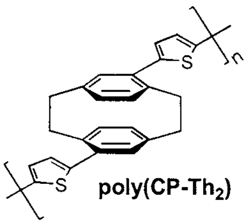
substituted α-thienyl positions to afford films of black electroactive polymer (**poly(CP−Th$_2$)**) on the electrode

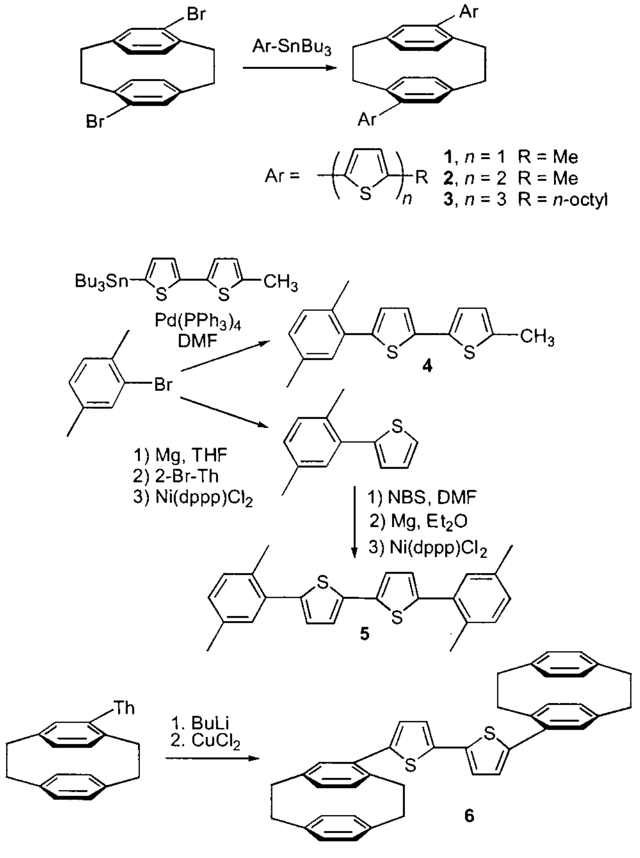

CP-Th$_2$


poly(CP-Th$_2$)

surface.[13] The irreversibility of the voltammetric peaks for these compounds led us to examine model compounds **1**−**6**. In contrast to previously reported thienyl-substituted cyclophanes, compounds **1**−**3** are substituted at the α-thienyl positions to block polymerization at these sites. The electrochemistry of xylene- and cyclophane-substituted bithiophenes **4**−**6** provides additional evidence for the electronic interaction between stacked delocalized cation radicals.

Bis(α-alkyloligothienyl)paracyclophanes **1**−**3** were prepared by Stille coupling of pseudoparadibromo-[2.2]paracyclophane[14] with appropriately substituted oligothienyltributylstannanes in the presence of Pd(PPh$_3$)$_4$,[15] Scheme 1.

Scheme 1. Synthesis of Paracyclophane and Xylyl-Substituted Oligothiophenes **1**−**6**



Coupling of appropriate oligothiophenes, xylenes, and cyclophanes gave compounds **4**−**6**. In general, Stille couplings proceeded to high conversion (70−80% crude yields). However, isolation of analytically pure products have not been yet been optimized and yields are typically <40%. ^{1}H NMR of thienyl-substituted cyclophanes at room temperature indicates free rotation around the cyclophane−thiophene bond transforming the structures between diastereomeric conformations. However, **CP−Th$_2$** crystallizes into a lattice with similar populations of two conformers in which the five-membered thiophene rings, which are tilted with respect to the phenylene rings, are rotated by 180° relative to one another.

Cyclophanes **1**−**3** undergo oxidation at slightly lower potentials than the unsubstituted analogues by virtue of the electron-donating nature of the alkyl substituents, Table 1.

Table 1. Redox and Spectroscopic Characterization of **1**−**8**

	electrochemistry		absorbance[f]
	E_{ox}/V[a]	no. of e$^-$	λ_{max}/nm (10^3 ε cm^{-1} M^{-1})
CP−Th$_2$	(+1.25)[b,c]		290 (22.5)
poly(CP−Th$_2$)	+1.00[c]		380[g]
1	(+1.18)[b]		
2	+1.05[d]	1 + 1	351 (54)
	+1.15[d]		
	+1.45[d]	2	
3	+0.95[d]	2	400 (63)
	+1.33[d]	2	
4	+1.12[d]	1	337 (22.5)
	+1.53[d]	1	
5	+1.10[d]	1	350 (27.5)
	+1.59[d]	1	
6	+0.98[e]	1	380 (16.7)
	+1.25[e]	1	

[a] CH$_2$Cl$_2$ (1 mM) containing 0.1 M Bu$_4$NPF$_6$, v = 100 mV/s on a platinum electrode; all values are given vs SCE; onset irreversible. [b] Peak onset, irreversible. [c] From ref 11. [d] $E_{1/2}$; reversible. [e] Quasireversible. [f] Solution in CHCl$_3$. [g] Thin film of electrochemically deposited polymer on ITO glass.

For example, **CP−Th$_2$** shows an onset of oxidation (polymerization) at +1.25 V versus SCE, relative to a value of +1.18 V for the dimethyl analogue **1**.[13]

The electrochemistry of the methyl-substituted bithiophene derivative **2** shows the influence of π-stacking on the redox activity of these oligothienyl-substituted paracyclophanes. The cyclic voltammogram of **2** shows two reversible two-electron oxidation waves at ca. +1.10 and +1.45 V for the sequential oxidation of each triaryl segment to the bis(radical cation), **2**$^{2(+\bullet)}$ (a model for stacked polarons), and then to the bis(dication), **2**$^{2(2+)}$ (stacked bipolaron). However, the voltammetric wave for the first oxidation is clearly broadened

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and split into two separate one-electron peaks at +1.05 and +1.15 V. This effect is more pronounced upon analysis by differential pulse voltammetry (DPV, Figure 1A), which has previously been used to study metal-containing mixed-valence systems.[16] This splitting is not observed in the voltammogram of unstacked xylyl analogue **4**, which undergoes oxidation to form the radical cation, $\mathbf{4}^{+\bullet}$, followed by subsequent oxidation to form the dication, $\mathbf{4}^{2+}$, reaction 1. Thus, the appearance of two separate one-electron oxidation peaks for **2** provides evidence for the mutual electronic influence of the π-stacked arenes. Removal of a single electron from one of the triaryl units of **2** to form a mono(radical cation), $\mathbf{2}^{+\bullet}$, is *facilitated* by the stacked oligoarene, which serves as an electron donor, reaction 2. Removal of an electron from the second triarene to form the bis(radical cation), $\mathbf{2}^{2(+\bullet)}$, is then *impeded* by the electron-withdrawing effect of the stacked radical cation. Splitting is not observed for the voltammetric wave of the subsequent oxidation to form the bis(dication), $\mathbf{2}^{2(2+)}$. Attributing these electronic effects to the influence of π-stacking is consistent with calculations that indicate that the differences in electronic structure between xylene and paracyclophane can be ascribed primarily to through-space interactions rather than to different inductive effects or to the twisting of the phenylene rings in [2.2]paracyclophane.[17]

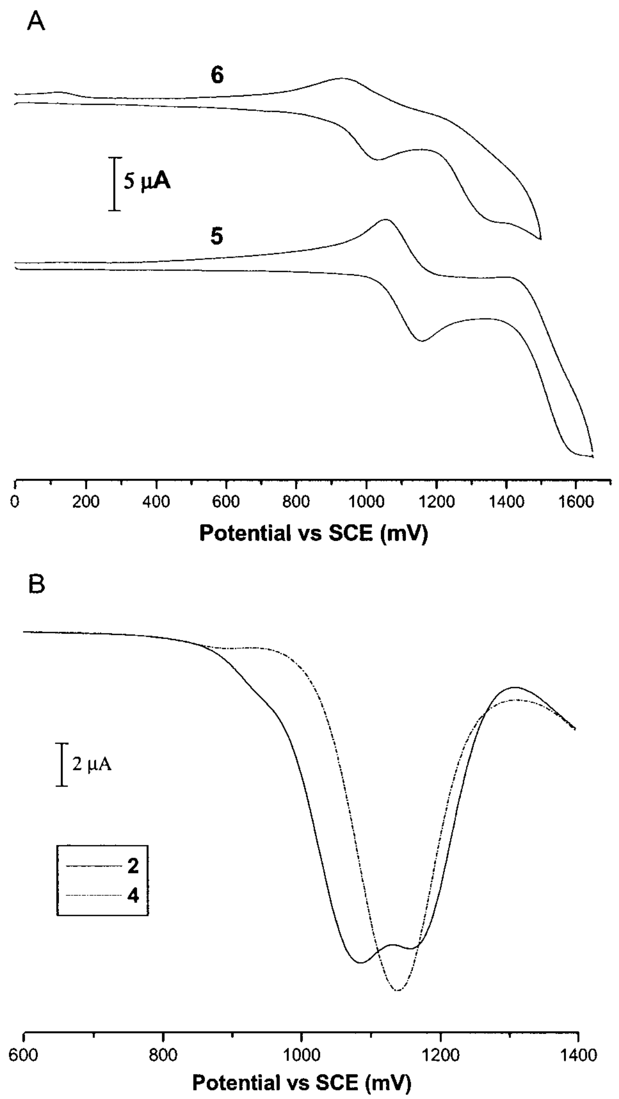

Figure 1. (A) Differential pulse voltammograms of **2** and **4**. (B) Cyclic voltammograms of **5** and **6** (1 mM in CH_2Cl_2 containing 0.1 M Bu_4NPF_6, v = 100 mV/s on a platinum electrode).

$$\mathbf{4} \rightarrow \mathbf{4}^{+\bullet} \rightarrow \mathbf{4}^{2+} \qquad (1)$$

$$\mathbf{2} \rightarrow \mathbf{2}^{+\bullet} \rightarrow \mathbf{2}^{2(+\bullet)} \rightarrow \mathbf{2}^{2(2+)} \qquad (2)$$

The splitting of the voltammetric wave for oxidation of identical stacked subunits was not observed in studies of other systems.[3,9] Splitting is also not observed for the terthienyl analogue **3**, which shows a sharp reversible two-electron voltammetric wave at +0.95 V and a second two-electron wave at +1.33 V. We interpret this difference in terms of the inherent stability of the tetraaryl radical cation of **3** arising from its extended conjugation, which renders it less electron demanding than the triaryl radical cation of **2**. Thus, electronic coupling between stacked conjugated subunits is most pronounced when the units are relatively short (**2** vs **3**). The bis(5-methylthienyl)-substituted analogue **1** undergoes electrooxidative polymerization even though the α-positions are blocked (presumably via $\beta-\beta$ coupling).

Cyclophanes bearing electron-donating groups undergo oxidation at lower potentials than monomeric model compounds.[9] The effects of π-stacking on the redox properties of thiophene oligomers are also apparent in the electrochemistry of aryl-substituted bithiophenes **5** and **6**, which were prepared as model compounds for the conjugated tetraaryl unit in **poly(CP−Th$_2$)**. The polymer displays a reversible oxidation wave at +1.0 V corresponding to formation of the stacked tetraaryl radical cation in the backbone.[13] The cyclic voltammogram of **6** exhibits two quasireversible one-electron redox waves with $E_{1/2}$ of +0.98 and +1.25 V, corresponding to oxidations to form a radical cation that is similar in structure to that formed by the polymer followed by formation of the dication (Figure 1B). The unstacked xylyl analogue **5** also shows two reversible redox waves. However, the stacked analogue **6** undergoes its first oxidation at a potential that is 120 mV lower than the unstacked xylyl model **5**. The effect of stacking is more pronounced for the second oxidation where the stacked analogue **6** undergoes oxidation at a potential that is 340 mV lower than that for **5**.

The effect of π-stacking on the absorption spectra of oligothiophenes is small. For example, **CP−Th$_2$** exhibits an absorption maximum at 290 nm, which is only slightly shifted from the maximum for the unstacked analogue,

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2-thienyl-*p*-xylene (280 nm). As expected, the absorption maximum of **6** is similar to that of **poly(CP−Th$_2$)** (380 nm), which has the same tetraaryl chromophore. However, the absorption maxima of these stacked chromophores are red shifted by 30 nm relative to the maximum of the unstacked analogue **5** ($\lambda_{max} = 380$ nm). In contrast to the relatively small effects of stacking on the absorption spectra of the thienyl-phenylene chromophores, the fluorescence of **CP−Th$_2$** (stacked dimer, $\lambda_{fl} = 405$ nm) is red shifted by 45 nm relative to thienyl-*p*-xylene (unstacked model, $\lambda_{fl} = 360$ nm), which is consistent with Bazan's observation on PPV derivatives in which an exciton undergoes energy transfer to a "phane state"[10] from which emission takes place. The red shift of the stacked dimer relative to the unstacked model becomes smaller as the conjugation length of the chromophore increases: emission of bithienyl-substituted analogue **2** is red-shifted by ca. 20 nm from the emission of unstacked model **4**.

In conclusion, the electronic interaction between oligoarenes held in permanent stacks is apparent from the electrochemistry and spectroscopy. Splitting of the first voltammetric oxidation wave of oligothienyl-substituted cyclophanes into two single-electron processes, together with their red-shifted fluorescence, illustrates the influence of π-stacking on the behavior of neutral and charged conjugated chains. Further studies will concentrate on the effect of the extent of overlap, distance, and orientation of charged conjugated units on their properties and their suitability as models for charge carriers in solid conjugated polymers.

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