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Stacked Conjugated Oligomers as Molecular Models to Examine Interchain Interactions in Conjugated Materials

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Face-to-face stacking of conjugated oligomers and polymers is a key characteristic of organic semiconducting materials. Studies of conjugated oligomers afford insight into the electronic properties of conjugated polymers and provide materials with potential for use in devices (e.g., FETs and LEDs).[1,2] However, characterization of linear oligomers in solution does not necessarily address the influence of intermolecular interactions on the electronic structure of conjugated systems in thin film devices. Observation of the reversible formation of π-dimers of radical cations of oligothiophenes in solution led to the suggestion that analogous spinless interchain radical cation π-dimers may be responsible for charge transport in conjugated polymers.[3−5] While the effect of molecular structure on the formation of π-dimers has been explored under a variety of conditions, details of the structure of these aggregates have not been firmly established.

Computational studies provide some insight into the evolution of electronic structure upon proceeding from a single one-dimensional conjugated chain to a 3D solid-state material. These studies examine the electronic structure of the neutral, cationic (i.e., radical cations), and dicationic forms of isolated oligomers, cofacial dimers, and stacks.[6−9] However, there remains a paucity of experimental molecular models to validate these computational approaches. A recent report on the electronic structure of quinquethiophenophanes was restricted to variation of the length of the bridging units between the termini of quinquethiophene units.[10] Here we explore the influence of interchain interactions on the properties of a series of oligothiophenes held in a cofacial arrangement by a bicyclo[4.4.1]undecane core,[11] *st*-$[Th_n]_2$ (Figure 1C). Examination of the stacked oligomers and linear (i.e., unstacked) models by voltammetry and absorption spectroscopy establishes the stabilization of mono- and bis(radical cation)s by interaction of the conjugated oligomeric tiers.

Bisthieno-fused bicyclo[4.4.1]undecanone **1** was prepared by alkylation of dimethyl 1,3-acetonedicarboxylate with 3,4-bis(bromomethyl)thiophene followed by saponification and thermal decarboxylation.[11] Ketalization with ethylene glycol locks the bicycloalkane into a chair−chair conformation in which the thiophene rings are stacked atop one another. This results in an upfield shift in the ^1H NMR signals of the α-thienyl protons (δ 7.00 for ketone **1**; δ 6.51 for ketal **2**) and appearance of a pair of sharp doublets of doublets for the benzylic protons. The X-ray crystal structure of **2** confirms that the thiophene units are held in a stacked orientation with a centroid-to-centroid distance of 359 pm, comparable to common π-stacking distances observed in solid polyarenes (the S−S distance is 429 pm, with an angle of 28° between the thiophene rings). Installation of conjugated arms on the bisthieno-fused bicyclo[4.4.1]undecanone core is straightforward. Tetrabromination of ketone **1** followed by Stille coupling with an appropriate thienyl stannane ($CH_3Th_m{-}SnBu_3$)[12] followed by ketalization provides stacked analogues of terthiophene (*st*-$[Th_3]_2$, $m = 1$) and quinquethiophene (*st*-$[Th_5]_2$, $m = 2$).

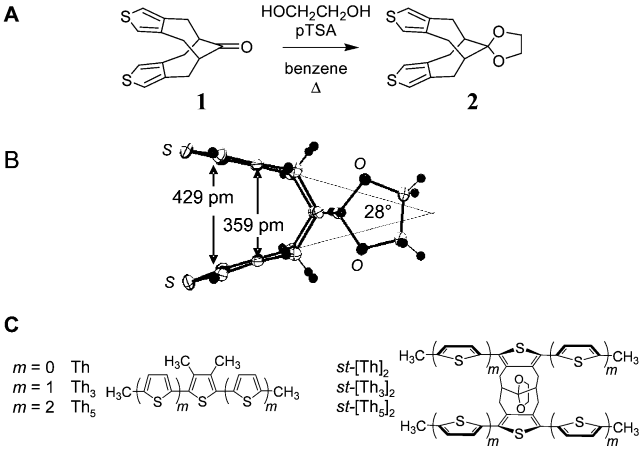

Figure 1. (A) Ketalization of bisthieno-fused bicyclo[4.4.1]undecanone. (B) X-ray crystal structure of **2**. (C) Model dimethyl-substituted linear oligomers, Th_n, and stacked oligomers, *st*-$[Th_n]_2$.

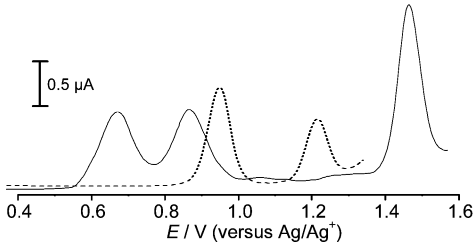

Figure 2. Differential pulse voltammograms (DPV) of *st*-$[Th_3]_2$ (solid line) and Th_3 (dots).

Stacking has a dramatic effect on the redox properties of oligothiophenes. Tetramethylthiophene, Th_1, exhibits an irreversible oxidation at +1.39 V, while the stacked analogue *st*-$[Th_1]_2$[13] undergoes two separate $1e^-$ oxidations at +1.09 and +1.59 V. Thus, whereas the first oxidation to form the mono(radical cation) is facilitated by stacking, removal of the second electron is impeded by Coulombic repulsion between the charged aromatic tiers.

Similarly, oxidation of the stacked terthiophene undergoes significant splitting upon stacking: Th_3 undergoes a reversible $1e^-$ oxidation at +0.96 V, whereas *st*-$[Th_3]_2$ undergoes two $1e^-$ oxidations, *both of which are at* lower potentials than the unstacked analogue (+0.70 and +0.90 V; Figure 2). This splitting and lowering of the oxidation potential is also observed for the stacked quinquethiophene *st*-$[Th_5]_2$ (Figure 3), which in contrast to Otsubo's observation that the first oxidation peak of quinquethiophenophanes is not split. The fact that the two $1e^-$ oxidations of the stacked analogue take place at lower potentials than the $1e^-$ oxidation of the linear analogue suggests that both the mono(radical cation) and dication are stabilized by the stacking interaction. In particular, lowering of the second $1e^-$ oxidation potential to form the dication

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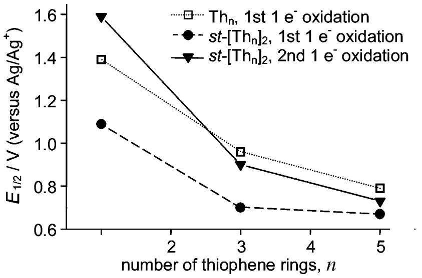

Figure 3. Plot of oxidation potentials of linear (Th$_n$) and stacked analogues (*st*-[Th$_n$]$_2$).

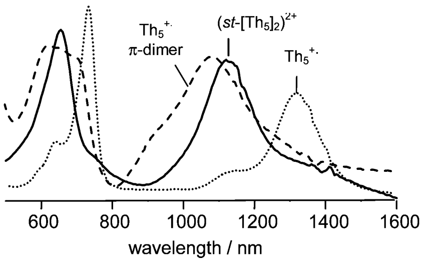

Figure 4. UV−vis−NIR spectra: dication of *st*-[Th$_5$]$_2$ (solid line); π-dimer of Th$_5$ formed upon cooling the radical cation to −30 °C in acetonitrile (dashes); and radical cation of Th$_5$ (dots).

suggests that the stacked dication is stabilized in such a way that it overcomes the destabilization that might be expected to arise from Coulombic repulsion.

The linear terthiophene and quinquethiophene undergo a second oxidation to form corresponding dications; the stacked analogues also undergo subsequent oxidation to form tetracations. This latter process takes place without splitting and at higher potential than for the linear analogues (Figure 2), which may be ascribed to stabilization of the stacked dication and to destabilization of the tetracation through Coulombic repulsion.

The electronic structure of the stacked dication and origin of this stabilization become apparent from UV−vis−near-IR and ESR spectroscopies. Oxidation of model Th$_5$ with FeCl$_3$ in CH$_2$Cl$_2$ affords the radical cation that gives rise to characteristic absorptions at 731 and 1322 nm (Figure 4). Cooling this solution leads to diminishment of these peaks with the appearance of new peaks at 620 and 1085 nm, consistent with the reversible formation of π-dimers.[5,14] Removal of 2 e$^-$/mol from the stacked analogue *st*-[Th$_5$]$_2$ gives peaks at 654 and 1123 nm, consistent with the formation of a stacked dicationic species with a similar electronic structure as the π-dimer. Addition of up to 2 equiv of FeCl$_3$ gives rise to the appearance of a signal in the ESR spectrum corresponding to the spin active mono(radical cation). However, this signal diminishes upon addition of more oxidant with formation of the spinless stacked dicationic π-dimer. This stacked dication is stable at low concentrations and at room temperature by virtue of the covalent linkage between the conjugated tiers. Similar behavior is observed in the linear and stacked terthiophenes, Th$_3$ and *st*-[Th$_3$]$_2$ (Table 1).

Table 1. Spectral Characteristics of Linear Oligothiophene Radical Cations and π-Dimers, and Analogous Stacked Dications

	cationic species	λ_{max}/nm[a]
Th$_3$	radical cation[a]	563, 884
	radical cation π-dimer[b]	460, 725
st-[Th$_3$]$_2$	dication[a]	506, 778, 970 (CT)[c]
Th$_5$	radical cation[a]	731, 1322
	radical cation π-dimer[b]	620, 1085
st-[Th$_5$]$_2$	dication[a]	654, 1123

[a] Generated by addition of FeCl$_3$ to CH$_2$Cl$_2$ solution of Th$_n$ or *st*-[Th$_n$]$_2$ at room temperature; [analyte] = 10^{-5} M. [b] Formed upon cooling to −30 °C in acetonitrile. [c] Weak charge transfer band (ref 5).

The absorption spectra indicate the similarity of the electronic structures of the dication of stacked conjugated oligothiophenes and radical cation π-dimers of linear analogues formed in solution. The accessibility and stability of both the mono- and dicationic states of the stacked analogues arise from the stabilizing influence of interchain interactions between conjugated radical cations. The splitting of the first two oxidations of the stacked oligomers gets progressively smaller as the conjugation length increases, consistent with the formation of a spinless charge carrier delocalized over a number of chains in a p-doped polymer film. Arene-fused bicyclo[4.4.1]undecanes provide a versatile scaffold to explore the effects of π-stacking on the electronic structure of a variety of other oligomers to provide models for a diverse set of conjugated polymers. The stacked mono(radical cation)s and dications serve as better models for polarons and bipolarons, respectively, than linear unstacked oligomers.

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Supporting Information Available: Characterization data, ^{1}H NMR spectra of **1** and **2**, ESR spectra of *st*-[Th$_5$]$_2$, and crystallographic information (CIF) for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) The spectrum of the mono(radical cation) of *st*-[Th$_5$]$_2$ consists of peaks at 440 (π−π* transition, red shifted from 386 nm for the neutral compound), 560, 670, and 1307 nm. The peaks at 560 and 760 nm arise from configuration mixing between electronic states as discussed by Brédas (ref 8).

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