

# $\pi$ -Dimers and $\pi$ -Stacks in Solution and in Conducting Polymers

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## Introduction

This Account describes research in organic chemistry and materials chemistry, research which is focused on a specific type of intermolecular bonding between the  $\pi$ -systems of ion radicals. Our strategy was to study ion radicals in solution and to use this knowledge to develop and understand electrically conducting polymers. We discovered an unusual phenomenon, the formation of  $\pi$ -stacks in solution, and developed some understanding of the molecular qualities which promote this phenomenon. These stacks are interesting because  $\pi$ -electrons are delocalized among the molecules in the stacks, sometimes leading to electrically conducting materials. In fact our studies led to the invention of new conducting polymers, such as the first conducting dendrimers, and polymers with unusual humidity-dependent and highly anisotropic (directional) conductivity. Studies of oligomer cation radicals in solution have also implicated  $\pi$ -aggregates as structural features in conducting polymers such as oxidized polythiophenes. These aggregates are important for understanding how electrons move from chain to chain in the conduction process.

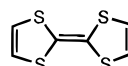
The solution phase studies described here lie in a burgeoning context (only leading references are provided throughout this Account) of studies on molecular self-assembly. Pertinent examples are dye aggregates,<sup>1</sup> porphyrin and phthalocyanine aggregates and polymers,<sup>2</sup> columnar liquid crystals,<sup>3</sup> and donor–acceptor complexes.<sup>4</sup>  $\pi$ -Stacks of ion radicals and mixed stacks of neutrals and ion radicals are well known in crystalline materials.<sup>5</sup> Indeed, much of the work described here can be considered an application of the concepts and methods developed for these crystalline electrical conductors. In general it is found that conductivity requires that the stacks be mixed valence, i.e., partially oxidized or reduced. This can be achieved by crystallization of mixed valence salts, e.g., (TTF)<sub>3</sub>(BF<sub>4</sub>)<sub>2</sub>, or charge transfer salts in which there are segregated stacks of the partially oxidized and the partially reduced compounds, e.g., TTF and TCNQ.<sup>5</sup>

## Aggregation of Imide Anion Radicals

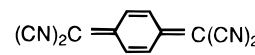
Our work on  $\pi$ -dimers and  $\pi$ -stacks evolved from studies of “molecular lines”, oligoimides composed

Larry L. Miller gave a graduate student seminar in 1964 at the University of Illinois entitled “Ion Radicals”. One of the concluding sentences of the extended abstract was “Little is known about the aggregation of ion radicals.” He has worked on a variety of topics in several institutions since then, but only recently returned to this one.

Kent R. Mann began his graduate career at Caltech in 1973 by investigating the solution aggregation of Rh(I) complexes. At the University of Minnesota he has studied spectroelectrochemistry, the photochemistry of metal arene complexes, and, most recently, organometallic materials chemistry.

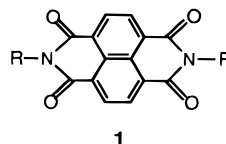


TTF



TCNQ

from naphthalene dianhydride and benzidines, which are rigid, linear, and up to 80 Å long. Molecules of this type were formed into self-assembled monolayers and Langmuir–Blodgett films, and allowed the length of a single molecule, a molecular line terminated with metal clusters, to be measured with an electron microscope.<sup>6</sup> Diimide **1a**, synthesized as a model for



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- 1a** R = SO<sub>3</sub><sup>-</sup>  
**1b** R = H  
**1c** R = N<sup>+</sup>-CH<sub>3</sub>  
**1d** R = N<sup>+</sup>-CH<sub>2</sub> Ph

amphiphilic molecular lines, was reduced by Jean Francois Pennneau to its radical anion (**1a**<sup>-</sup>).<sup>7</sup> Using one-electron electrochemical or sodium dithionite reduction in water, he found a strong band at 1140 nm in the near-infrared (near-IR) region. This band, which was absent from the spectrum of **1a**<sup>-</sup> in DMF solution, was interpreted as a charge transfer (CT) band, polarized along the axis of the intermolecular  $\pi$ -bond of a  $\pi$ -dimer. Shifts in the  $\pi$ - $\pi^*$  bands, diminished ESR intensities, and measurement of equilibrium constants confirmed the formation of a  $\pi$ -dimer in which one anion radical was stacked on top of the other. Figure 1 shows how the SOMO orbitals of ion radicals such as **1a**<sup>-</sup> mix to give the  $\pi$ -bond and the CT band of  $\pi$ -dimers.

Several ion radical  $\pi$ -dimers are known,<sup>8</sup> discovered and studied by means of the CT absorption found in polar solvents. These polar solvents are logically

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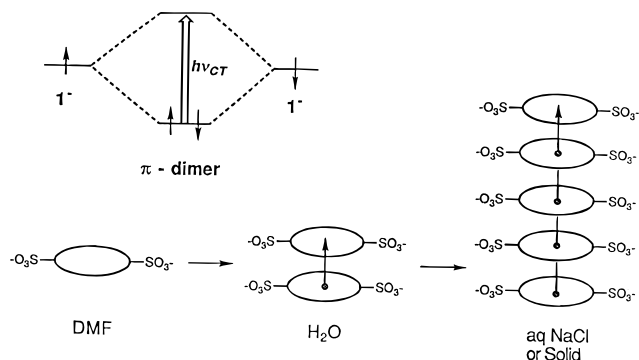
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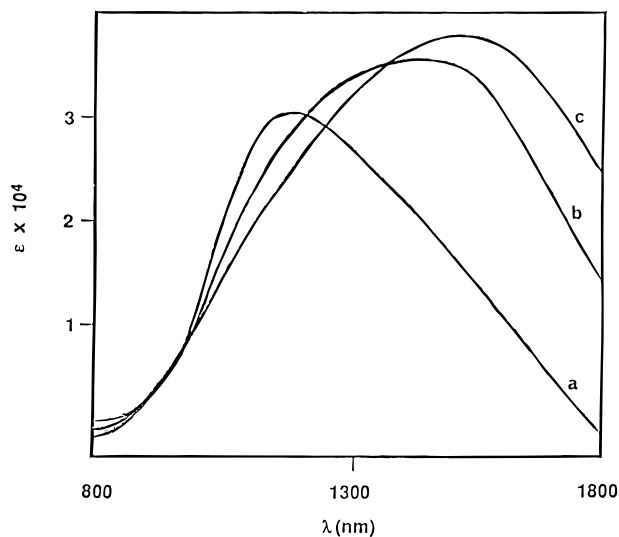
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**Figure 1.** Schematic of  $\pi$ -dimerization and  $\pi$ -stacking. Perturbation diagram showing mixing of SOMOs to form new orbitals of the  $\pi$ -dimer.

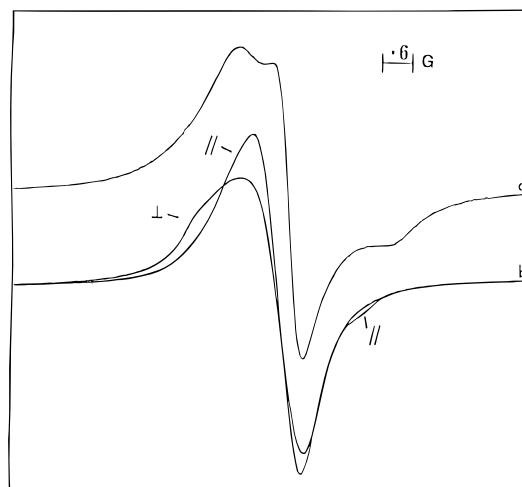


**Figure 2.** Near-IR spectra of  $1a^-$  in 0.5 M aqueous NaCl. Concentration of  $1a^-$ : (a) 0.43 mM, (b) 2.1 mM, (c) 4.3 mM.

necessary to stabilize the like charges on the ion radicals that come together in the dimer. Similarly, it is known that cationic dye molecules, typically cyanine dyes, aggregate in water to form dimers and higher aggregates.<sup>1</sup> Because these dyes are closed shell molecules, there is not a new long-wavelength band due to charge transfer, but there are significant spectral shifts in the  $\pi-\pi^*$  bands. Dye aggregation is known to be enhanced in salt solutions and by higher dye concentrations.

When NaCl was added to aqueous solutions of  $1a^-$  or the concentration of  $1a^-$  was increased, the near-IR spectrum showed even longer wavelength absorptions (Figure 2), which grew in at the expense of dimer intensity at 1140 nm. It was proposed that higher aggregates,  $\pi$ -stacks, were formed.  $\pi$ -Stacks had not been documented for ion radicals in solution, so we precipitated  $1a^-$  as a sodium salt ( $1a^-$  is actually a trianion because of the sulfonates) and measured its spectra. Interestingly it formed an air stable thin film that was fragile, but could be studied intact or ground up to form a powder. The absorption spectrum of the solid had near-IR absorption that extended into the IR, and both vis and IR spectra were consistent with expectations for stacks of anion radicals.

Significantly, the ESR spectra of aggregated  $1a^-$  in solution were weak (most of the spins are paired in the aggregates) and anisotropic (Figure 3). Indeed, these spectra corresponded closely to the spectrum observed for a powdered sample of the solid. Such



**Figure 3.** ESR spectra of  $1a^-$ : (a) 8 mM in 0.5 M aqueous NaCl, (b) thin film, ( $\perp$ ) with a thin dimension perpendicular to the magnetic field, ( $\parallel$ ) with one long dimension parallel to the magnetic field

anisotropic spectra result from radicals that rotate slowly on the ESR time scale and in solution are logically assigned to aggregates. The intact film of  $1a^-$  held perpendicular or parallel to the applied field gave ESR spectra which could be interpreted in terms of stacks which were preferentially oriented in the film plane.

To understand more about the aggregation process, several naphthalene diimide anion radicals, e.g.,  $1b^-$ – $1d^-$ , were studied. We expected, for example, that cationic substituents on nitrogen might lead to reduced Coulombic problems and better aggregation. Anion radical  $1c^-$ , indeed, had longer wavelength absorbance (1700 nm) than  $1a^-$ . It was considered that a significant contribution to the aggregation was from the hydrophobic segregation of organic and aqueous microphases, and we found that  $1d^-$  with benzyl rather than methyl substituents gave  $\lambda_{max} = 2050$  nm. Mixing together  $1a^-$  and  $1c^-$  with cationic and anionic substituents led to evidence for a mixed aggregate. There was a strong dependence of the  $\lambda_{max}$  on the mole ratio of the two anion radicals, with the longest wavelength absorbance at a 1:1 mole ratio of  $1a^-$  to  $1c^-$ .<sup>9</sup>

The solid state literature names this long-wavelength near-IR/IR band the optical conduction band.<sup>10</sup> It is an electronic transition due in ion radical salts to excitation of  $\pi$ -electrons along the stack (see Figure 1). It is expected that the delocalization length will determine the wavelength of absorption, just as in ordinary  $\pi$ -systems like polyenes, where the delocalization is intramolecular. Although changes in stack structure can affect optical spectra,<sup>11</sup> the evidence in this case strongly supports the conclusion that stack size primarily determines the near-IR transition energies.

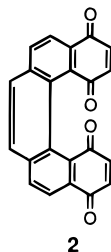
These diimides showed no optical bands attributable to  $\pi$ -dimers or stacks formed from dianion aggregation or from mixed-valence neutral/anion radical aggregation. For example, a solution of  $1a^-$  that was half-reduced had a vis/near-IR spectrum identical in shape and position to that of the fully reduced compound plus

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(11) Exstrom, C. L.; Sowa, J. R., Jr.; Daws, C. A.; Janzen, D.; Moore, G. A.; Stewart, F. F.; Mann, K. R. *Chem. Mater.* **1995**, *7*, 15.

the neutral compound, but with half the intensity for each. As discussed below, mixed valence aggregation is observed in polymer films where the concentration is higher, and in the helicene diquinone anion radical  $2^-$ <sup>12</sup> where the two quinones are stacked rigidly together.<sup>17</sup>



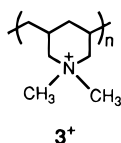
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In toto, these studies gave strong support to the idea that  $\pi$ -stacks form in solution and gave us the tools to study a variety of related problems. We took it as our task to connect these results to materials science by preparing polymer films in which diimide anion radicals would provide a pathway for conductivity.

### Diimide Polymer Films

Conducting polymers formed from anion radicals are considered n-doped (negatively doped). Such polymers are extremely rare because they are not air stable. Therefore, the air stability of the precipitated films of  $1a^-$  made it of special interest to make polymeric materials. Because there are very few examples of conducting polymers in which isolated electrophores attached to polymers form the conducting network, we initially took a conservative approach, embedding diimide anion radicals into a polymer matrix. This method is attractive<sup>13</sup> because one has the possibility to obtain a film with the mechanical properties of the host polymer and the electrical properties of the embedded small molecules.

Following previous work on the electroprecipitation of single crystals of small molecules,<sup>14</sup> Chuan-Jian Zhong<sup>15</sup> electrochemically deposited a polymer film by reducing  $1a$  in an aqueous solution of polycation  $3^+$ .

3<sup>+</sup>

A shiny, black film formed on the electrode, which was the composite of  $1a^-$  and  $3^+$ . Air stable free-standing films had vis, near-IR and IR spectra quite similar to the solution and film spectra of stacked  $1a^-$  described above.

Conductivity measurements along the film plane showed that the conduction was electronic, not ionic. In dry argon, the conductivity along the film plane was  $\sigma = 10^{-4} \text{ S cm}^{-1}$  ( $1 \text{ S} = 1 \text{ } \Omega^{-1}$ ). At 90% humidity  $\sigma = 10^{-1} \text{ S cm}^{-1}$ . It was shown gravimetrically that the films took up water from the air, so that somehow the

conductivity, even though it was electronic, was enhanced by the diluent, water.

Another unusual aspect of the conductivity was the high anisotropy. At 90% humidity, the ratio of  $\sigma$  in the plane to that across the film was greater than  $10^6$ . To our knowledge such a high anisotropy is unprecedented. The structural origin of this anisotropy was explored using linearly polarized near-IR spectra and, with Paul Kasai from IBM, ESR spectra of samples oriented in the spectrometers. It was concluded that  $\pi$ -stacks were present and preferentially oriented in the film plane. This provided an explanation of the observed anisotropy of the conductivity, since these stacks would conduct electrons along the film plane, but interstack electron transfer would limit the conductivity across the film.

Intrigued by these results, we set out to develop simpler, film casting methods to form conductors. We chose to cast films of  $1a^-$  or  $1c^-$  in poly(vinyl alcohol) (PVA).<sup>16</sup> For chemistry done on earth, water is the solvent of choice, and since PVA is an excellent nontoxic film former, the combination was attractive. For example,  $1c$  was reduced with 1.1 equiv of sodium dithionite in a mixture of PVA and water, and polymer films were spin cast under argon at 65 °C. Observation with an optical microscope revealed no evidence for precipitated particles or microcrystals, and no diffraction lines were observed from X-ray diffraction. The threshold for conductivity was about 3 wt % loading of  $1c$  in PVA. At 10 wt %,  $\sigma = 10^{-3} \text{ S cm}^{-1}$ . These films were again quite anisotropic in terms of conductivity and spectra. This emphasized that the stack structure, not the matrix, led to the anisotropy.

Casting allowed the composition of the film to be controlled in ways not possible with electroprecipitation, and this allowed a careful look at the correlation of near-IR and ESR spectra with conductivity. Using films of  $1a^-$ , each reduced with 1.1 electrons per diimide, it was found that higher loading with anion radicals gave more intense and longer wavelength near-IR bands and higher conductivity, as expected. Importantly, reduction with 0.55 electron per diimide gave films with even higher conductivity and more intense optical conduction bands. This was the first evidence for mixed-valence diimide stacks containing both neutral and anion radicals in the stacks. Theory holds that mixed valence is required for high conductivity in crystalline ion radical salts.<sup>5</sup>

Recently, we set out to study conducting polymers which have diimides covalently attached to a polymer chain. For this study we used unusual, hyper-branched polymers, dendrimers. Dendrimers are built up by sequential synthesis of larger and larger generations with branch points in each generation. Although we expected that linear polymers might form conducting films, the three-dimensional shape of higher generation dendrimers seemed to provide some unusual structural features and materials chemistry possibilities. We imagined delocalization of electrons, not just in linear stacks but around the periphery of the dendrimer in a manner somewhat reminiscent of a fullerene.

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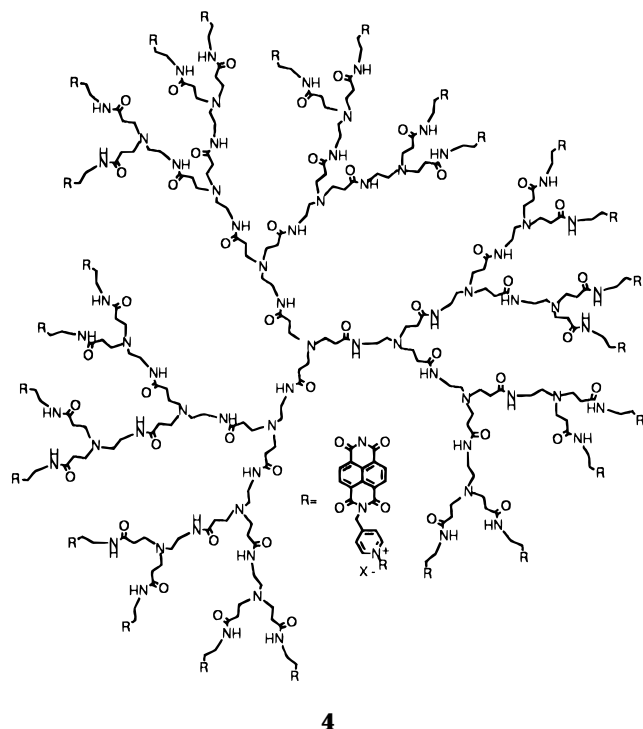
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Poly(amidoamine) (PAMAM) dendrimers, developed by Donald Tomalia and his co-workers,<sup>17</sup> were peripherally modified with diimide moieties, providing products such as **4**, which were highly loaded with diimide



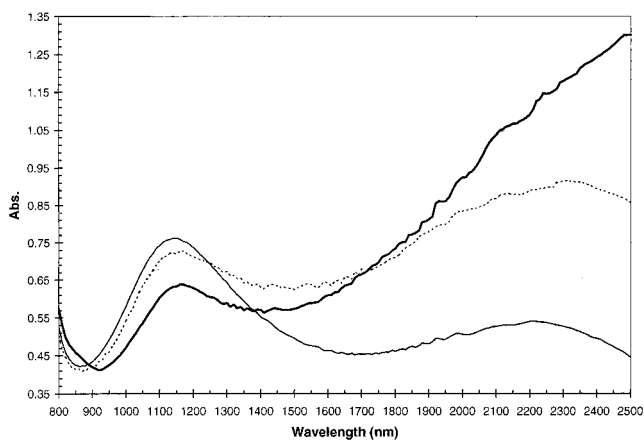
groups.<sup>18</sup> Reduction with dithionite in water gave soluble products with up to 192 anion radicals per molecule, and near-IR studies showed that aggregation into stacks occurred as expected. Somewhat unexpected was the similarity of the near-IR spectra for all the generations 2–6. This result demonstrated that the PAMAM scaffold had little effect on the aggregation phenomenon. Cyclic voltammograms of these dendrimers were also extremely similar to each other. Ibro Tabakovic showed that at the one-electron reduction level, the reduced dendrimers are precipitated on the electrode as a conductive layer that can be stripped anodically. A more detailed analysis suggested the presence of mixed-valence stacks.<sup>9</sup>

Using the generation-3 modified polymer **4** (24 diimide groups) reduced with dithionite, films were cast from formamide on glass under reduced pressure at elevated temperature.<sup>19</sup> The conductivity and optical and ESR spectra of the films were isotropic. This shows that on the molecular and macroscopic levels there is a three-dimensional interaction between stacks unlike the directional quality found for small molecule films. The conductivity was humidity dependent, and at 95% humidity, a mixed-valence film (0.55 electron per diimide) showed  $\sigma = 11 \text{ S cm}^{-1}$ . Again, partially reduced, mixed-valence films had stronger optical conduction bands (Figure 4) and were more conductive than fully reduced ones. Unexpectedly, these conductivity values are higher than those for pure diimide anion radical salts, which have a much higher concentration of anion radicals.

The humidity dependence of the conductivity was discovered when Robert Duan breathed on the film,

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**Figure 4.** Near-IR spectra of films of **4**: fully reduced film cast at 120 °C (solid line) and at 60 °C (thin dashed line); partially reduced film cast at 60 °C (thick dashed line).

causing the electrical resistance to rapidly decrease. When he stopped blowing, the resistance returned to the original value. The effect was studied using a quartz crystal microbalance in a controlled humidity environment, and evidence for plasticization due to water uptake was found.<sup>9</sup> Plasticization effects on the rate of stack-to-stack electron transport could account for increased conductivity. If this relationship between plasticization and higher conductivity is at all general, it could have interesting implications for the future development of conducting polymers.

### Oxidized Oligothiophenes

Although oligothiophenes have device applications,<sup>20</sup> the focus here will be on more fundamental aspects of the structure and physical properties of their cation radicals and dications, especially  $\pi$ -aggregation. This was of particular interest because it provided an opportunity to study  $\pi$ -dimerization as a function of oligomer length and structure. Also of interest are correlations of the optical spectra of the various oligomeric cations, and comparison of these results with the properties of oxidized, conductive polythiophenes.

Because of their ease of synthesis and stability, many alkyl- and alkoxy-substituted polythiophenes are known, and several have been well characterized.<sup>21–23</sup> Oxidized electrochemically or chemically, these polymers often have conductivities on the order of  $10^2 \text{ S cm}^{-1}$ . The structure and conductivity of these materials is understood in terms of polarons and bipolarons.<sup>21–24</sup> Briefly, polarons are cation radicals localized to a segment of one chain (about four thiophene rings); bipolarons are the corresponding diamagnetic dications. Because oxidized polythiophenes usually have a low spin count, bipolarons are often proposed to be the species primarily responsible for conduction. Thus, the conduction process is thought

(20) Roncali, J. *Chem. Rev.* **1992**, *92*, 711.

(21) (a) *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vols 1 and 2. (b) *Conjugated Polymers*; Bredas, J. L.; Silbey, R., Eds.; Kluwer: Dordrecht, The Netherlands, 1991. (c) *Conjugated Polymers and Related Materials*; Salaneck, W. R.; Lundstrom, I.; Ranby, B., Eds.; Oxford University Press: Oxford, 1993.

(22) See Chen, T. A.; Wu, X.; Rieke, R. R. *J. Am. Chem. Soc.* **1995**, *117*, 233. Zotti, G.; Gallazi, M. C.; Zerbi, G.; Meille, S. V. *Synth. Met.* **1995**, *73*, 217.

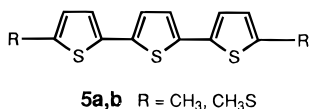
(23) Heeger, A. J.; Smith, P. In ref 21b, pp 141–210.

(24) Chung, T. C.; Kaufman, J. H.; Heeger, A. J.; Wudl, F. *Phys. Rev.* **1984**, *B30*, 702. Heeger, A. J.; Kivelson, S.; Schrieffer, J. R.; Su, W. P. *Rev. Mod. Phys.* **1988**, *60*, 782.

to involve bipolaron migration along chains and electron hopping from chain to chain. It is the interchain structure that is of interest to us here.

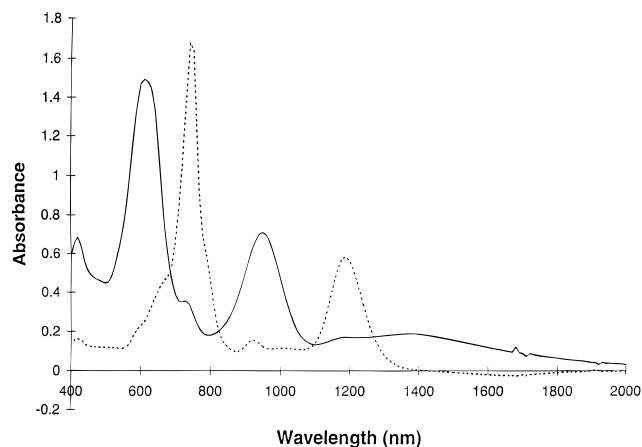
### Oligothiophenes in Solution

The first oxidized oligothiophenes with stable cation radicals were produced by the anodic oxidation of 3-methoxythiophene.<sup>25</sup> This study, as well as practical experience with the electrochemical switching of polypyrroles,<sup>26</sup> led us to investigate well-defined oligomers that had stable cation radicals and dication. Using methyl- and thiomethyl-substituted oligomers such as **5a,b** with blocked terminal positions, Mike Hill showed



that in methylene chloride solution the ESR active cation radicals and ESR silent dication species were sufficiently stable so that their optical spectra could be recorded using spectroelectrochemistry.<sup>27</sup> More extensive synthetic efforts by other researchers with corresponding CV and vis studies<sup>28–34</sup> confirmed that blocking the terminal positions prevented polymerization, and using methylene chloride as solvent, they documented the spectra of neutral cation radical and dication species for oligomers made soluble by alkylation that had as many as 12 thiophene rings. The cation radicals showed two  $\pi-\pi^*$  bands at wavelengths much longer than those of the neutral compounds. The dication showed one  $\pi-\pi^*$  band, located in between the two bands of the cation radical. As expected the  $\pi-\pi^*$  absorption bands moved to longer wavelength as the molecules increased in length, approaching an asymptotic limit similar to the wavelength found for oxidized polythiophenes.

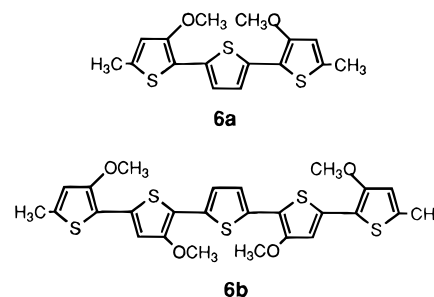
When oligothiophene cation radicals are formed in the more polar solvent acetonitrile, new absorption bands appear which can be assigned to intermolecular  $\pi$ -dimers.<sup>27,28</sup> The  $\pi$ -dimers showed three bands, two  $\pi-\pi^*$  bands shifted to shorter wavelength compared to the undimerized species and a CT band at longer wavelength in the near-IR. As expected for diamagnetic dimers, the ESR signal intensity was small in



**Figure 5.** Vis/near-IR spectra of **6b**<sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub> (dashed line) and CH<sub>3</sub>CN (solid line).

acetonitrile. No evidence for dimers of dication or mixed neutral/cation radical dimers was found.

Dimerization equilibrium constants were measured by Baruch Zinger and Yuan Yu for the cation radicals of **5a,b** and alkoxy-substituted oligomers, e.g., **6a,b**



(Figure 5).<sup>35</sup> It was shown that  $\pi$ -dimer formation was enhanced for longer oligomers;  $K_{\text{DIM}} > 10^3 \text{ mM}^{-1}$  for the pentamer **6b**, and  $K_{\text{DIM}} = 0.7 \text{ mM}^{-1}$  for the trimer **6a**. Furthermore, by studying oligomers with hydrogen, methyl, or phenyldimethylsilyl on the terminal positions, it was shown that there was no significant steric effect on dimerization. We speculate that “twisted dimers” which minimize the effects of the bulky terminal substituents are relatively stable. The propensity for  $\pi$ -dimerization of larger cation radicals was also emphasized by Bauerle and co-workers who studied a series of alkyloligothiophenes in methylene chloride at low temperature.<sup>33</sup>

$\pi$ -Dimers have now been found under other interesting circumstances. For example, the study of an oligomer with 12 rings led to the proposal that two cation radicals were formed on each molecule and that these dication species then  $\pi$ -dimerized.<sup>30b</sup> A study of the metastable products formed in a solid film of sexithiophene in an active light-emitting diode (LED) also revealed cation radical  $\pi$ -dimer formation.<sup>36</sup> This is significant because the oligomer film is neutral and these oxidized products are formed in only minute concentrations.

With oligothiophene  $\pi$ -dimers firmly established, we turned our attention to  $\pi$ -stacks. Since we had shown that TTF dicarboxylate cation radicals<sup>37</sup> stacked in

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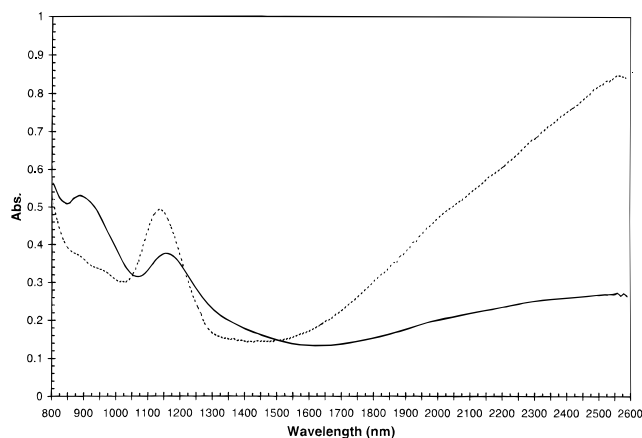
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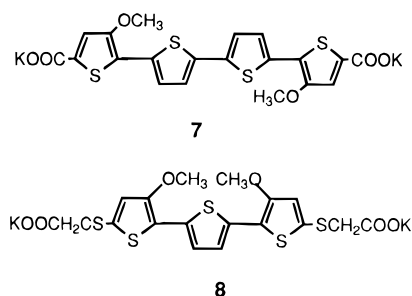
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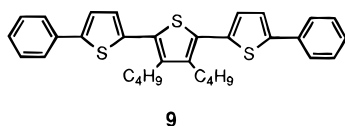
**Figure 6.** Near-IR spectra of  $7^+$  in KBr: solid line,  $1.15 \text{ F mol}^{-1}$  oxidation; dashed line,  $0.55 \text{ F mol}^{-1}$  oxidation.

aqueous solution, it was an obvious approach to synthesize and oxidize the carboxylate-terminated oligomers **7** and **8**.<sup>38</sup> In aqueous solution both  $7^+$  and



$8^+$  showed optical conduction bands that were indicative of stack formation. In the case of  $8^+$  this band shifted to longer wavelength when NaCl was added to the solution. Cation radical salts were isolated that showed solid state near-IR bands and proved to be electrically conductive. Partial oxidation (0.5 equiv of  $\text{I}_2$ ) of oligomer **7** gave higher conductivity and more intense optical conduction bands (Figure 6) than full one-electron oxidation.

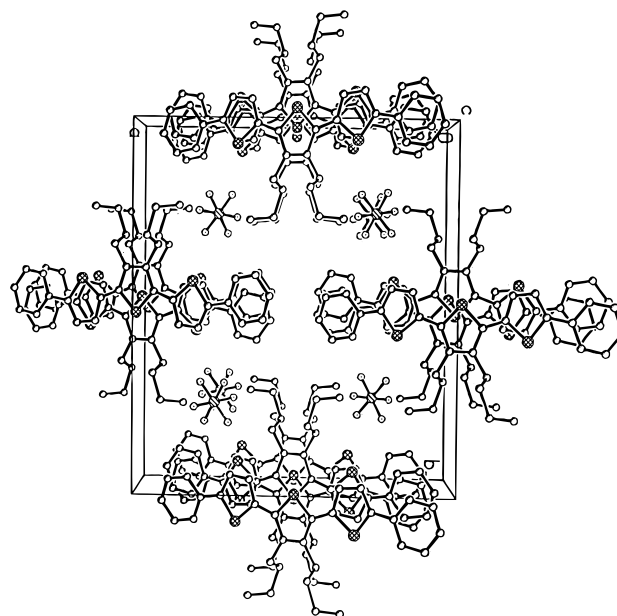
Although the data for imides, TTF derivatives, and oligothiophenes are quite self-consistent and support the hypothesis of  $\pi$ -stack formation, we have until recently been unable to confirm this with a crystal structure. This has now been remedied by Dave Graf who has obtained the X-ray structure of the oxidized dibutylphenylterthiophene  $9^+$ .<sup>39</sup> Electrochemical oxidation of **9** in methylene chloride deposited crystals



on the electrode with the composition  $9^+, \text{PF}_6^-$ . The structure (Figure 7) shows stacks of ion radicals slightly slipped to give a bond-over-atom arrangement. The optical spectra of the solid were as expected and included the optical conduction band in the near-IR/IR region. The conductivity along the needle (stack) axis was  $10^{-2} \text{ S cm}^{-1}$ .

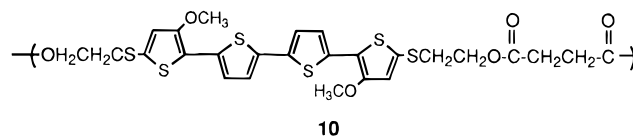
### An Oligothiophene Polymer and Polythiophenes

To more directly test the hypothesis that  $\pi$ -stacks can be important in polymer conductivity, Yaoliang



**Figure 7.** Crystal structure of  $9^+, \text{PF}_6^-$ .

Hong prepared the polyester **10** which has oligothio-



phene units isolated in the main chain.<sup>40</sup> Because it does not have continuously conjugated chains, this polymer cannot conduct via polarons or bipolarons. It can, however, form  $\pi$ -dimers and  $\pi$ -stacks. The polyester was synthesized by condensation of the appropriate dialcohol and diacid chloride and characterized by combustion analysis, NMR, IR, UV, and gel permeation chromatography. Oxidation was performed with iodine or ferric chloride in methylene chloride. Optical and ESR spectra demonstrated that cation radicals were formed and, indeed, suggested that stacks were formed in solution. Thin films of **10** were cast from methylene chloride onto glass and then oxidized with iodine. As oxidation proceeded over time the conductivity increased, eventually reaching  $0.8 \text{ S cm}^{-1}$ . A strong optical conduction band and weak ESR signal were recorded. Stability was established by reducing the film to give back the original polymer, unchanged. This polymer, which cannot have bipolarons, exhibits good conductivity, and ESR and optical spectra that are quite similar to those of oxidized polythiophenes.

It is well recognized that interchain electron transport is necessary for conductivity in polymers.<sup>21,24</sup> Indeed, since this process can limit the rate of electron transport, it is important to understand the intermolecular structure of these materials. We suggest specific  $\pi$ -dimer and  $\pi$ -stack structures, essentially aggregates of polarons. Since such structures form at millimolar concentrations in solution, they should form in solids where the concentrations are very much higher. The fact that longer oligomer cation radicals dimerize better further supports the speculation that

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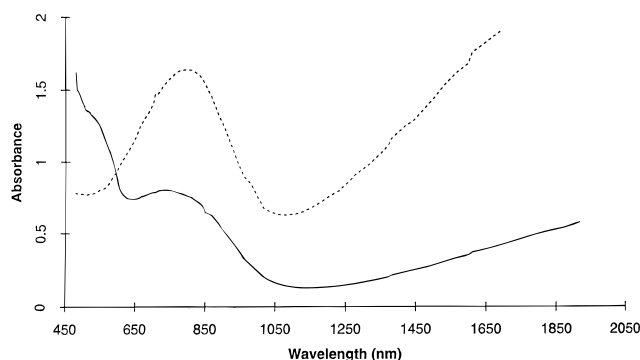
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$\pi$ -dimers or even stacks will form in oxidized polymers like polythiophenes. While it is true that higher conductivities are often found for oxidized polythiophenes ( $\sigma = 10\text{--}10^3$ ) than we have found for oligothiophene salts or polymer **10**, those conductivities are substantial and a larger oligomer salt has been reported to have  $\sigma = 20\text{ S cm}^{-1}$ .<sup>41</sup> The formation of discrete interchain aggregates makes the problem of understanding conductivity in conjugated chain polymers a three-dimensional problem instead of the much simpler one-dimensional problem addressed by polaron–bipolaron theory. Intermolecular aggregates provide a pathway for electron transfer between chains, but on the other hand these structures might have a localizing effect on electron transport along the chains.

Theoretical studies are now appearing concerning the  $\pi$ -dimer/bipolaron problem. They are of two types: general descriptions of interchain interactions<sup>42</sup> that we would identify as  $\pi$ -dimers and specific calculations on cation radicals and dications as models for polarons and bipolarons.<sup>43</sup> High-quality molecular orbital calculations of  $\pi$ -dimer structures have not to our knowledge appeared, but there are many theoretical descriptions of bonding in ion radical  $\pi$ -stacks.<sup>5,10</sup>

$\pi$ -Dimers have recently been invoked to explain the voltammetry and spectra of polythiophenes formed from bridged bithiophenes.<sup>44</sup> Of particular interest here, however, is the ESR and optical spectroscopy of more typical polythiophenes.<sup>21,23</sup> The low ESR spin count of oxidized polythiophenes has been interpreted in terms of bipolarons, but  $\pi$ -aggregates can equally well account for the data. The near-IR data collected during oxidation of polythiophenes show two new bands that grow in as oxidation proceeds beyond about 1 electron per 100 rings. These bands have been assigned to bipolarons, but Figure 6 shows that  $\pi$ -aggregates give similar spectra. We note that oligomeric dications, bipolaron models, have only one absorption band in the near-IR.

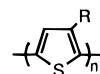
The difficulty in unraveling intra- and interchain structures is well illustrated by spectra obtained when poly(3-hexylthiophene) was oxidized in methylene chloride.<sup>45</sup> Near-IR bands (Figure 8), which are extremely similar to those found for solid films, built up as the oxidation proceeded. The ESR spin count was quite low, also comparable to that found in thin films. Since the solutions were dilute, it was considered that the results originated from single-chain structures, and this gave strong support to bipolarons formed in solution and in the solid. However, since polymer **10** and even oligothiophenes form cation radical  $\pi$ -aggregates in dilute solution, it is reasonable that oxidized poly(3-hexylthiophene) would do the



**Figure 8.** Near-IR spectra of oxidized poly(3-hexylthiophene) in  $\text{CH}_2\text{Cl}_2$ : solid line, 0.03 electron per thiophene; dashed line, 0.2 electron per thiophene. Data from ref 45 are digitized and plotted.

same. Interchain aggregates would have spectra (see Figure 6) quite comparable to those observed.

Of further interest are X-ray diffraction studies on stretch-oriented, iodine-oxidized poly(3-alkylthiophenes).<sup>46</sup> Analysis of X-ray data for the unoxidized



Poly(3-alkyl thiophene)

polymers led to a postulated structure for the crystalline regions which has linear polythiophene chains lined up and stacked with a spacing of 3.7–3.8 Å. Oxidation led to a sharp decrease in scattering intensity, but the peak corresponding to chain stacking was found even for highly oxidized samples, indicating that  $\text{I}_3^-$  did not intercalate into the stacks. The position of this peak shifted slightly as oxidation proceeded, indicating that the distance between thiophene chains became shorter. We interpret this result to be consistent with interchain  $\pi$ -bonding.

In summary the study of oligothiophenes as models for the structural entities in polythiophenes has produced evidence for  $\pi$ -aggregation of oxidized chains. Understanding these structures is essential for understanding conductivity.

## Predictions

We believe that  $\pi$ -aggregates will generally be found for ion radicals if the medium is properly chosen and that aggregation will be enhanced for larger molecules. The similarity of structural elements (oxidized chains of rings and/or double bonds) and spectra of other conducting polymers to those of polythiophenes further suggests that  $\pi$ -aggregates will be important for understanding a variety of conducting polymers. In this Account we have tried to reveal the intertwined process of chance discovery and careful experimental design that leads to both better understanding and new materials. Hopefully, this has illustrated that intermolecular thinking is a useful approach to the practice of organic/materials chemistry.

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