CHAPTER 4

Semiconducting Materials Based on Polyelectrolyte Templated Polyaniline and Tetrathiafulvalene
Papers published

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4.1 INTRODUCTION

Several classes of organic charge transfer complexes, ion-radical salts and conjugated polymers have been investigated which show electrical properties ranging from semiconductivity to superconductivity. In Sec. 1.4 we have briefly discussed various classes of conducting materials and the properties exhibited by them. Polymer systems with special properties constitute a field of increasing scientific and technological interest offering synthetic chemists an opportunity to develop a broad variety of new materials. In chapters 2 and 3 we have investigated several novel chromophores and NLO-phores with covalently attached but remote functionalities that strongly influence the molecular assembly. This led to the discovery of a variety of interesting phenomena and the fabrication of novel optical and nonlinear optical materials. We have extended this logic to the control of molecular assembly through the utilization of template structures and the fabrication of semiconducting molecular and polymeric materials providing insight into the correlation of molecular organization and materials attributes. In this chapter we present our explorations in this direction leading to the fabrication of novel semiconducting molecular materials.

In Sec. 4.2 we explore a simple synthetic protocol for the development of stable aqueous colloidal solutions of poly(4-styrenesulfonate) templated polyaniline. The electrical conductivity and submicro/nano features observed in their spin coated films are shown to be correlated to the polyelectrolyte template molecular weight. This study demonstrates the utility of the polyelectrolyte template as a new design element for conducting polymer films.

In Sec. 4.3 we present the synthesis and conductivity studies of a new class of molecular materials which incorporate tetrathiafulvalene (TTF) and polyionic polymers such as poly(4-styrenesulfonate), poly(vinylsulfate) and poly(4-styrenesulfonate-co-maleic acid). Enhancement of the conductivity by $\sim 10^2 - 10^4$ over the starting TTF salt was observed in these new materials. We present also the interesting crystal structure of the pentacarbomethoxy cyclopentadienide (PMC) salt of TTF. This complex is found to have an unusual 2-dimensional structure wherein trimerized segregated stacks of TTF run in orthogonal directions forming a square grid. The counterions form a sheath structure
around the core made up of the TTF stacks. Single crystal conductivity studies reveal anisotropic character consistent with the TTF organization.  

4.2 POLYELECTROLYTE TEMPLATED POLYANILINE - FILM MORPHOLOGY AND CONDUCTIVITY

Polyaniline (PANI) is one of the most extensively studied materials among the conducting polymers. The reasons for this are manifold. Synthesis of PANI is simple and facile, through chemical as well as electrochemical means, and the polymer shows a high degree of chemical stability. It is conveniently doped using protons to achieve a wide range of optical characteristics and conductivities, facilitating applications ranging from sensors to smart windows. Recently PANI and its composites have been shown to exhibit several submicro and nano architectures which have significant impact on the materials attributes. The basic problems of solubility and processability of PANI have been addressed through approaches such as self-doping, choice of different counterions and templating. The latter technique employing polyelectrolytes is particularly successful in improving aqueous solubility and hence is significant from the point of view of environmental considerations and processing methodology. It has been suggested that polyelectrolytes serve as nanoreactors during the enzymatic oxidative polymerization of aniline. It is of considerable interest to establish correlations between features of the polyelectrolyte template and the electrical conductivity of the film so that new design strategies can be evolved.

We have developed a simple and convenient protocol for the synthesis of poly(4-styrenesulfonate) (PSS) templated PANI (along similar lines as reported in Ref. 23) and the fabrication of good quality films by adding trace amounts of polyvinyl alcohol (PVA). Interestingly, the electrical conductivity of the films is found to depend on the template molecular weight. Scanning electron microscopic examination of the films reveals submicro and nano level features which depend on the molecular weight of the PSS used and the amount of the PVA additive, providing insight into the morphology dependence of the electrical conductivity. Many of the microscopic characterizations of
soluble PANI in earlier work were on the colloidal state\(^{22-24}\) or on bulk powders.\(^{15,25}\) We have focused attention on the films which would be of direct relevance to most of the practical applications. Our study highlights the role of the template molecular weight as a design element in the fabrication of conducting PANI.

**Synthesis and characterization**

PANI-PSS was synthesized in aqueous solution by the oxidative polymerization of aniline using ammonium peroxodisulfate and hydrochloric acid in presence of poly(sodium 4-styrenesulfonate) (NaPSS). NaPSS with average molecular weights, 100 kDa and 70 kDa were used; the resulting polymers will be denoted respectively as PANI-PSS-100 and PANI-PSS-70. The 100kDa polymer was obtained from Acros Organics and the 70kDa polymer from Aldrich Chemical Co. Aniline was distilled twice under reduced pressure. Millipore Milli-Q water (resistance = 18 MΩ) was used in all preparations. 0.42 ml (4.6 mmol) aniline was added to 15 ml of 3M hydrochloric acid. 2.78 g (13.5 mmol of monomer) of NaPSS dissolved in 13 ml of water was added with continuous stirring over 10-15 min. The entire solution was cooled to 0 - 5°C and 1.02 g (4.4 mmol) of ammonium peroxodisulfate dissolved in 8 ml of water was added dropwise over 20 - 30 min. The solution was stirred for 2.5 h to complete the polymerization. The final solution diluted with water (total weight = 43 g) was subjected to dialysis (dialysis bags with 50 kDa cut-off were boiled with EDTA and NaHCO\(_3\) prior to use) with aqueous HCl (pH = 4) changed every 20 min, three times. The dialyzed colloidal solution (weight = 48 g) was centrifuged for 90 - 120 min with the supernatant water removed and replaced with fresh water three times during this period. 17 g of the colloid was diluted by adding 10 ml of water and sonicated for 15 min. 7 g of the resulting solution was mixed with different weights (0.032, 0.064, 0.096, 0.128 g) of aqueous solutions of PVA (1.13 g PVA dissolved in 10 ml water).

Samples in the form of KBr pellets were made from vacuum dried PANI-PSS for FT-IR spectra. The spectra of PANI-PSS-100 and PANI-PSS-70 are similar. The peaks at 1561 and 1487 cm\(^{-1}\) are characteristic of the C=C stretching vibration of the quinononoid and benzenoid rings respectively. The bands at 1294 and 1238 cm\(^{-1}\) correspond to C-H...
bending vibrations. These peaks are similar to those reported earlier. The PANI produced in our synthesis protocol is in the emeraldine salt form. UV-Vis spectra of the PANI-PSS show, besides the 355 run and 418 run peaks, the polaron absorptions. The polaronic bands of the colloidal solutions and spin coated films of PANI-PSS-70 show peaks at 783 nm and 706 nm respectively. Addition of PVA has no effect on the former, but causes a further blue shift to 693 nm in the latter. The blue shift observed on film formation possibly arises due to the rigidification of the polymer chains restricting polaron delocalization to smaller segments, which is further enhanced in the film containing PVA. PANI-PSS-100 similarly shows the band maxima at 820 nm and 722 nm respectively in the colloidal solution and film. Once again, PVA addition causes a shift in the film alone, with the peak observed at 694 nm. The red shift observed for the solution and film of PANI-PSS-100 (with respect to PANI-PSS-70) signifies relatively longer conjugated segments with less kinks and defects, most likely facilitated by the formation of longer PANI chains. At present we cannot confirm this through the determination of the PANI molecular weight which is complicated due to the coexistence of the strongly bound polyionic chains in PANI-PSS.

**X-ray photoelectron spectroscopy**

Powder samples of PANI-PSS can be obtained by precipitation on addition of acetone or methanol to the colloidal solution or by removal of the water under dynamic vacuum. The dried powder compactions were characterized by XPS analysis. The instrumentation details are provided in Appendix A and the significant data are presented in Table 4.1. The N(1s) peak is normally deconvoluted into three, with the lowest one at ~ 399.5 eV assigned to neutral amine/imine sites and the higher ones at > 400 eV assigned to protonated N, their exact identities still being a matter of discussion. We have deconvoluted the N(1s) peak into two, representing the unprotonated and protonated states (Fig. 4.1); the relative intensities indicate the extent of protonation of PANI in PANI-PSS-100 and PANI-PSS-70 to be respectively 0.64 and 0.54. The relatively high values suggest protonation of the imine as well as amine N sites, promoted possibly by the polymeric sulfonic acid template formed from the PSS in the acid medium; it may be noted that even higher protonation levels have been reported for polyaniline-
Table 4.1 Selected XPS data for PANI-PSS films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak/eV [atom %]</th>
<th>Protonation level of N</th>
<th>Atom % SO₃H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S</td>
<td>N</td>
<td>NH⁺</td>
</tr>
<tr>
<td>PANI-PSS-100</td>
<td>168.37 [8.20]</td>
<td>399.06 [0.93]</td>
<td>401.02 [1.66]</td>
</tr>
</tbody>
</table>

polyelectrolyte complexes. The XPS analysis rules out the presence of Cl but indicates that Na is present in PANI-PSS, implying that SO₃⁻ groups on the PSS chains are associated with H⁺, NH⁺ and Na⁺. The composition of SO₃⁻H⁺ (x_{SO₃⁻H⁺}) can be inferred from the atomic percentages of sulfur (x_S), all of which exists in the form of SO₃⁻, protonated nitrogen (x_{NH⁺}) and sodium ions (x_{Na⁺}), by imposing the charge balance, x_S = (x_{SO₃⁻H⁺} + x_{NH⁺} + x_{Na⁺}); the values are presented in Table 4.1. Based on this, the relative amounts of the amine and sulfonate groups in the protonated state i.e. x_{NH⁺}/x_{SO₃⁻H⁺} can be estimated. Interestingly this ratio appears to be quite similar (~ 0.8 - 0.9) in the two polymer samples indicating that the same equilibrium controls the proton distribution in both.

**Thin film fabrication and conductivity**

The polymer films were fabricated by spin coating on glass plates or pieces of aluminum foil. The glass plates were cleaned with detergent followed by high purity water and *iso-propyl* alcohol and dried in a hot air oven at 90°C. 1 cm² pieces of aluminum foils were cleaned by rubbing with acetone and dried in hot air oven. Typical spinning speeds and times employed for the spin coating were 2000 rpm and 30 sec. Films of PANI-PSS were fabricated using the colloidal solutions directly or after mixing with small amounts of aqueous PVA solution. Four different blends were prepared
Figure 4.1 The N(ls) peaks in the XPS spectrum of (a) PANI-PSS-100 and (b) PANI-PSS-70; the smoothed experimental data (•), the fit using multiple Gaussian functions (—–), and the deconvolution (—–—–) are shown.
containing 0.046, 0.092, 0.138 and 0.184 weight % of PVA. The PVA addition makes the colloids stable for several months. The colloids are spin coated to form films. PANI-PSS without PVA additive does not coat well beyond a single layer. Interestingly, addition of the trace amount (~ 0.05 weight %) of PVA vastly improves the film quality and facilitates fabrication of multiple coatings. The coated films were dried under dynamic vacuum for 10 h and then in a hot air oven at 80°C for 1 h before conductivity measurements or SEM study discussed later. The films are quite uniform, as revealed by the smooth scaling of the film thickness (determined by viewing the film cross section in an SEM) with the number of layers coated. We find that the average thickness of a single layer is ~ 270 nm.

PANI-PSS without any PVA additive where only single layers could be coated, showed high resistance; therefore conductivity could not be measured reliably. However, 4-probe conductivity measurements (details are given in Appendix D) could be carried out on thicker films (15 layers on glass) of PANI-PSS containing different amounts of PVA. The conductivity changes very little with the PVA composition in the case of PANI-PSS-100 and even less in PANI-PSS-70 (Table 4.2). This is primarily due to the fact that the quantity of PVA added is very small. It is also consistent with observations

<table>
<thead>
<tr>
<th>Weight % of PVA</th>
<th>a (10^{-2} \text{ S cm}^{-1}) (PANI-PSS-100)</th>
<th>a (10^{-2} \text{ S cm}^{-1}) (PANI-PSS-70)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.046</td>
<td>8.3</td>
<td>4.5</td>
</tr>
<tr>
<td>0.092</td>
<td>8.3</td>
<td>3.6</td>
</tr>
<tr>
<td>0.138</td>
<td>9.1</td>
<td>3.6</td>
</tr>
<tr>
<td>0.184</td>
<td>12.5</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Table 4.2 4-probe room temperature conductivity of PANI-PSS films containing different amounts of PVA additive.
that conducting polymers manifest self-assembly leading to little interference to the conducting pathways from the electrically insulating additive.\textsuperscript{921} The more significant observation presented in Table 4.2 is the sensitivity of the film conductivity to the molecular weight of the template polyelectrolyte; the higher molecular weight PSS leads to improved conductivity in the film. Together with the shift of the polaronic band with the molecular weight of the template noted earlier, this observation suggests that the polyelectrolyte acts as a nanoreactor template, controlling the polymerization process,\textsuperscript{21} the longer PSS chains promote the formation of more extended and possibly better aligned PANI chains.

\textit{Scanning electron microscopy}

We have examined the morphology of the films to gain insight into its influence on the conductivity. Though the morphological features are similar for films coated on glass and aluminum foil, the latter provided better clarity in general. Hence the micrographs presented are of films coated on aluminum foil substrates. Fig. 4.2 shows scanning electron micrographs of PANI-PSS-100. The influence of PVA addition is clearly visible. The morphology is nearly circular disc-like in the absence of PVA (Fig. 4.2a); the packing density is low since, as noted earlier, a single layer alone is coated. The shape resembles those observed in similar instances reported earlier\textsuperscript{22} and the diameter is approximately 250 - 350 nm. It turns into a distinct rod shape when 0.09 weight % of PVA is added (Fig. 4.2c). At this stage the rods are typically 80 - 100 nm wide and 220 - 400 nm long. As the PVA content is increased the rod length goes up to ~1 \textmu m with small increase in the average width (Fig. 4.2d). However the packing density is reduced at higher PVA content. The morphology of the PANI-PSS-70 are shown in Fig. 4.3. The trends with PVA addition are similar to those in the previous set, though less dramatic. More significantly the sizes of the different features are distinctly smaller. For example, the discs in Fig. 4.3a show average diameters in the range 30 - 60 nm and the rods in the case of films with 0.09 weight % of PVA (Fig. 4.3c) are typically 55 - 70 nm wide and 120 - 300 nm long. The former are slightly larger than the sizes reported earlier for PANI-PSS.\textsuperscript{23} At the highest PVA content, a mixture of rods and discs are observed.
Figure 4.2 Scanning electron micrographs of PANI-PSS-100 containing (a) 0.000, (b) 0.046, (c) 0.092, (d) 0.138 and (e) 0.184 weight % of PVA additive.
Figure 4.3 Scanning electron micrographs of PANI-PSS-70 containing (a) 0.000, (b) 0.046, (c) 0.092, (d) 0.138 and (e) 0.184 weight % of PV additive.
It is instructive to analyze the possible role of PVA in the morphology changes and its impact on the conductivity of the PANI-PSS films. In view of its extremely small mol ratio with respect to PANI-PSS, PVA is likely to be engaged only in some surface level molecular interactions with PANI-PSS aggregates. Such a picture is consistent with its stabilizing influence on the PANI-PSS colloid and further suggests that the assembly of the aggregate structures observed in the spin-coated films may be initiated in the colloidal state itself. The H-bond interactions between PVA and PANI/PSS chains at the periphery of the aggregates, possibly promotes an organized assembly leading to the rod-like morphology which becomes more prominent with increasing PVA content. The conductivity does not show any strong dependence on the percentage of PVA, which may be understood in terms of the simultaneous increase in the size of particles and decrease in their packing density. The higher sensitivity of the conductivity in the case of PANI-PSS-100 compared to PANI-PSS-70 is consistent with the larger morphology changes in the former, noted above. Compared to PANI-PSS-70, the extent of protonation in PANI-PSS-100 deviates more from the optimal 0.50. In spite of this, the latter shows higher conductivity which appears to result from the larger size of the features observed in these films. We infer that the longer PSS chains promote the growth of more extended PANI chains, eventually leading to larger features in the spin coated films. The parallel observed between the thin film conductivity and morphological characteristics points to the relevance of the template polymer molecular weight as a design element for the PANI chains.

4.3 POLYELECTROLYTE TEMPLATED TETRATHIAFULVALENE (TTF) AND THE 'CORE AND SHEATH' STRUCTURE OF A TTF COMPLEX

Planar organic molecules possessing delocalized π-electrons with good electron donating or accepting capabilities are important candidates for molecular conducting materials. Several families of organic donors and acceptors have been developed over the last three decades, which form molecular conductors and superconductors. However the single largest family of organic conductors is still based on TTF, one of the earliest n-electron donors. Several excellent reviews may be consulted for the extensive work
published on the TTF family of complexes.\textsuperscript{26} The versatility of TTF stems primarily from its unique electronic and structural features such as the electron rich planar \textit{n-system}, the stability of fractional oxidation states and the d-orbital electrons on the S atoms which enable interstack interactions. One of the significant factors that has contributed to the singular success of the TTF framework in forming crystalline complexes is the strong tendency it shows towards the formation of stacked structures. Neutral TTF itself has a stacked structure and a second polymorph discovered some years ago has been found to have a chain structure.\textsuperscript{27} TTF forms charge transfer and ion-radical complexes with a wide variety of molecules and counterions. The counterions used include simple inorganic anions such as halides,\textsuperscript{28} nitrate\textsuperscript{31} or thiocyanate,\textsuperscript{32} transition metal complexes\textsuperscript{33,34} and organometallics.\textsuperscript{35,36} Examination of the crystal structures of the TTF salts and complexes reveals a wide range of packing motifs with a predilection towards \textpi-stacking. The regular segregated stacked structure found in many systems\textsuperscript{32,34,37,39} including the prototypical TTF-TCNQ\textsuperscript{40} is most conducive to metallic conduction. Effects such as Peierl's instability\textsuperscript{41} often lead to dimerized\textsuperscript{42,43} or trimerized\textsuperscript{35,44,45} segregated stack structures; there is even an example with a pentamerized stack of TTF.\textsuperscript{46} Though uninteresting from the point of view of conducting materials, several TTF complexes show mixed stack structure incorporating the counterions in the TTF column.\textsuperscript{47} There exist also TTF complexes where isolated monomeric,\textsuperscript{34,48} dimeric\textsuperscript{36,49} or trimeric\textsuperscript{50} TTF’s are present.

A survey of these structural variations manifested by TTF complexes suggests that TTF based systems provide a fertile ground to explore novel stacking patterns. Strongly \textit{1-dimensional} structures are prone to low temperature instabilities such as Peierl's distortion that lead to metal-semiconductor transition. From the point of view of stabilizing the metallic state in molecular conductors \textit{2} and \textit{3-dimensional} structural motifs are important. Several polymeric materials containing TTF have been synthesized and characterized.\textsuperscript{51,52} Among those which show high conductivity,\textsuperscript{52,53} some are prepared by doping a polymer containing TTF with electron acceptor molecules and others involve the polymer itself as the electron acceptor. Exploration of molecular and polymeric materials based on TTF complexes continues to be a fruitful exercise as they provide new approaches to highly conducting molecular materials.
**Synthesis and conductivity studies of polyanion salts of tetrathiafulvalene**

We have considered the synthesis of polymeric salts of TTF where TTF\(^+\) is combined with polyanions. We envisaged that such systems would simultaneously develop an ordering of the polymer chains and stacking of TTF\(^+\) ions. The inherent tendency of TTF and its ions to stack would encourage the polymer chain to order and the spacing of the charge sites on the polyanion in turn would control the interplanar distances in TTF stacks. Mixed valence systems can form if appropriate amounts of TTF and TTF\(^+\) are incorporated in the stacks. We have utilized poly(4-styrenesulfonate) (PSS) in Secs. 2.4 and 4.2. In the following preliminary studies we have used PSS (with molecular weights 100 kDa and 70 kDa) as well as other polyanions such as poly(vinylsulfate) (PVS, MW = 170 kDa), 3:1 poly(styrene-co-maleic acid) (31PSSM, MW = 20 kDa) and 1:1 poly(styrene-co-maleic acid) (11PSSM, MW = 20 kDa) to form salts with TTF\(^+\).

A typical synthesis proceeds as follows. (TTF)\(_3\)(BF\(_4\))\(_2\) was synthesized following reported procedure.\(^{54}\) 0.1 gm (0.127 mmol) of (TTF)\(_3\)(BF\(_4\))\(_2\) was dissolved in distilled acetonitrile. A solution of 50 mg (0.231 mmol of monomer) of the sodium salt of PSS dissolved in 2 ml deaerated water was added to it. A brown colored precipitate separated out immediately. A tentative representation of the reaction is shown in Scheme 4.1. The product was filtered out washed with water and acetonitrile and dried under vacuum.

![Scheme 4.1](image)
M.P. = 250-260°C (dec); FT-IR (KBr) : ν/cm⁻¹ = 3418.1, 2926.3, 1352.2, 1122.6, 1032.0, 1005.0, 827.5. Fig. 4.4 shows the absorption spectrum of PSS salt of TTF (TTF-PSS-70). The spectrum shows the presence of neutral TTF (λ_max = 306 nm) as well as the cation, TTF⁺ (λ_max = 581, 435, 340 nm). Similar results were obtained with the other polyanions mentioned above. We have made extensive efforts to obtain reproducible compositional analysis of the materials prepared. However no satisfactory consistency could be achieved in this regard. We believe that this may be due to the randomness in the final composition of the polyanion and alkali metal counterions which comes with the polyanion. We have carried out 2-probe resistivity measurements on powder compactions of the final TTF complexes (see Appendix D for details). The resistivities show good consistency between several batches which were measured. The values obtained for the different polyanion complexes are collected in Table 4.3. The consistent decrease of the resistivity of the TTF⁺ complexes on incorporation of the polyanions points to the likelihood of improved stacking assembly of the TTF moiety in these materials.
<table>
<thead>
<tr>
<th>Complex</th>
<th>$\rho$ (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(TTF)$_3$(BF$_4$)$_2$</td>
<td>$10^7$ - $10^8$</td>
</tr>
<tr>
<td>TTF-PSS-100</td>
<td>$10^5$</td>
</tr>
<tr>
<td>TTF-PSS-70</td>
<td>$10^3$ - $10^2$</td>
</tr>
<tr>
<td>TTF-PVS</td>
<td>$10^4$</td>
</tr>
<tr>
<td>TTF-31PSSM</td>
<td>$10^4$</td>
</tr>
<tr>
<td>TTF-11PSSM</td>
<td>$10^4$</td>
</tr>
</tbody>
</table>

**Structure and conductivity of (TTF)$_3$(PMC)$_2$**

(TTF)$_3$(PMC)$_2$ was synthesized as reported earlier. We have characterized the elemental composition and crystal structure of this material. Stoichiometries like (TTF)$_3$X$_2$ with X being a monoanion and (TTF)$_3$X with X being a dianion are well known among TTF complexes. The stoichiometry implies an average partial ionicity of +0.67 on TTF which leads to metallic conductivity in the case of TTFCl$_{0.67}$ and TTF(SCN)$_{0.67}$. However, in several cases, trimerized TTF stacks are formed with concomitant localization of charge and reduced conductivity. The crystal structure analysis of (TTF)$_3$(PMC)$_2$ indicates that it belongs to the latter case. The crystallographic data are collected in Table 4.4. The C atoms were refined isotropically and only the S and O atoms were refined fully anisotropically in this structure. The asymmetric unit consists of three TTF molecules (Fig. 4.5a) and two PMC anions (Fig. 4.5b). The TTF molecules A and B almost eclipse each other and B and C are in the 'ring-over-bond' conformation. The molecules are nearly flat and parallel with average interplanar angle of 2.4° between A and B and 2.8° between B and C. The average interplanar distance between A and B is 3.435 Å and that between B and C is 3.427 Å; these distances are slightly shorter than the interplanar distance of 3.47 Å in TTF-TCNQ. The shortest S...S distances between A and B is 3.335 Å and that between B and C is 3.659 Å. The average interplanar distance between C and its neighboring A in the stack is 3.402 Å. The three interplanar distances indicate that the stack deviates only slightly from a
regular segregated stacking motif; it is probably best described as a weakly alternating stack of C-A dimers and B (Fig. 4.6). The stacking clearly suggests the likelihood of localization of charge on the TTF molecules.

The TTF stacks form layers parallel to the $ab$ plane. The stacks in one layer run along the $[110]$ directions while the stacks in the adjacent layers run in an orthogonal direction, namely $[110]$ forming a square grid structure. PMC form columns running along the $[110]$ and $[110]$ directions. The spacing between the mean planes of adjacent pentagons within the column is 10.738 Å ruling out any kind of $\pi$-stacking. The PMC columns running parallel to the TTF stacks and the layer of PMC with their molecular planes in perpendicular orientation together provide a sheath structure around the TTF stacks. Superposition of the core structure of TTF and the sheath structure of PMC ions leads to the 'core and sheath' architecture of the $(TTF)_3(PMC)_2$ crystal shown in Fig. 4.7.

### Table 4.4 Crystallographic data for $(TTF)_3(PMC)_2$.  

<table>
<thead>
<tr>
<th>Compound</th>
<th>$(TTF)_3(PMC)_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Formula</td>
<td>$C_{48}H_{42}O_{20}S_{12}$</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>1323.54</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>Cc</td>
</tr>
<tr>
<td>$a/A$</td>
<td>16.017(10)</td>
</tr>
<tr>
<td>$b/A$</td>
<td>14.307(12)</td>
</tr>
<tr>
<td>$c/A$</td>
<td>25.091(8)</td>
</tr>
<tr>
<td>$a/\text{deg}$</td>
<td>90.0</td>
</tr>
<tr>
<td>$\beta/\text{deg}$</td>
<td>92.11(3)</td>
</tr>
<tr>
<td>$\gamma/\text{deg}$</td>
<td>90.0</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
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<tr>
<td>$\mu/\text{cm}^{-1}$</td>
<td>5.3</td>
</tr>
<tr>
<td>$\rho_{\text{calc}}/\text{g cm}^{-3}$</td>
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</tr>
<tr>
<td>$\rho_{\text{meas}}/\text{g cm}^{-3}$</td>
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<tr>
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<td>Number of reflections with $I &gt; 2\sigma(I)$</td>
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<td>0.0514</td>
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<tr>
<td>$wR^2$</td>
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</table>
Figure 4.5 Molecular structures of (a) TTF trimer unit and (b) PMC dimer unit in (TTF)$_3$(PMC)$_2$ from single crystal X-ray analysis showing 10% probability ellipsoids on S and O atoms; H atoms are omitted for clarity.

Figure 4.6 Schematic representation of the TTF stacks in (TTF)$_3$(PMC)$_2$. 
Some of the short interatomic distances observed between the core and sheath structures are the following: S1...O68 = 3.117 Å, C19...O68 = 3.122 Å, C22...O58 = 3.200 Å, C26...O60 = 3.264 Å, C24...O70 = 3.266 Å and C21...O58 = 3.275 Å. The sheath of counterions around the TTF stack precludes interstack interactions and the 2-dimensional character which normally supports the formation of a metallic state. However, the novel case of TTF stacks running in orthogonal directions in \((TTF)_3(PMC)_2\) leads to a new kind of two-dimensional structural motif.

The 2-dimensional character of the grid network is reflected in the unusual resistivity anisotropy. DC resistivity measurements were carried out on single crystals in the form of rectangular plates. Measurements were made in the \([1\overline{1}0]\) and \([110]\) directions which were found to be along the long and short axes of the rectangular face respectively and in the \([001]\) direction, perpendicular to the rectangular face. The measured values are, \(p[1\overline{1}0] = 6.7 \times 10^4 \, \Omega \cdot \text{cm}\), \(p[1\overline{1}0] = 2.3 \times 10^5 \, \Omega \cdot \text{cm}\) and \(p[001] = 2.4 \times 10^6 \, \Omega \cdot \text{cm}\). The resistivity anisotropy in the orthogonal directions in the \(ab\) plane is about 3.4 whereas the anisotropy between the axes in the \(ab\) plane and the \(c\) axis are...
respectively 10 and 36. The semiconducting nature of (TTF)$_3$(PMC)$_2$ results from the small but definite trimerization present in the stack. ESR experiments carried out on a microcrystalline sample of (TTF)$_3$(PMC)$_2$ showed weak triplet exciton signals. This is consistent with the presence of neighboring localized TTF$^+$ radicals in the stack.

4.4 SUMMARY

We have developed novel semiconducting polymeric and molecular materials of polyaniline and tetrathiafulvalene by employing new synthetic strategies involving polyelectrolytes as templates for organizing the molecular assembly. In Sec. 4.2 we have presented the detailed synthetic protocol for (i) the preparation of stable colloidal solutions of PANI using the environmentally friendly aqueous route and (ii) the formation of good quality polyelectrolyte templated PANI films. The morphological characterization reveals interesting features at the submicro and nano levels and their sensitive dependence on the amount of the PVA additive. The investigation also reveals the correlation between the morphology and the electrical conductivity of the films. Preliminary studies in our laboratory suggest that these PANI-PSS films exhibit sensitive and fast resistivity change responses to the presence of ammonia vapors. Its sensor capabilities are currently under exploration.

In Sec. 4.3 we have demonstrated the enhancement of conductivity by $\sim 10^2$ - $10^4$ in various polyelectrolyte complexes of TTF over the precursor salt (TTF)$_3$(BF$_4$)$_2$. This suggests the possible symbiotic interaction between the $\pi$-donor molecular ions and the polyanionic polymer that leads to improved polymer chain alignment and $\pi$-stacking. Detailed characterization of these new materials is yet to be achieved. We have also presented the unusual square grid structure in (TTF)$_3$(PMC)$_2$ crystals, formed from the TTF stack cores and the PMC sheaths. The flat structure of the anions and their non-stacking nature has led to this new packing motif in the TTF complex. The trimerization observed in the TTF stacks is not very strong. Incorporation of suitable derivatives of the cyclopentadienide ion which support interaction between the cores of TTF stacks, could lead to complexes with similar architecture exhibiting novel 2-dimensional metallic conductivity.
REFERENCES


