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Production of a Polymer with Highly Anisotropic Conductivity and Structure by Co-Electroprecipitation of an Imide Anion Radical and Polycation

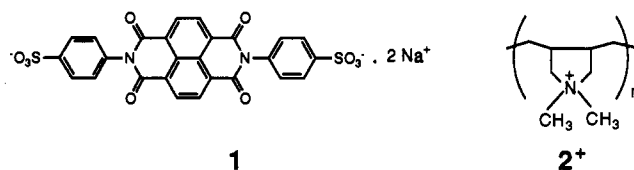Larry L. Miller,* Chuan-Jiang Zhong, and Paul Kasai†

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Abstract: Polymer films were grown by electroreduction on solid electrodes or a mercury surface from an aqueous solution containing disodium *N,N*-bis(*p*-sulfonatophenyl)naphthalenedicarboximide (1) and the cationic polymer poly-(diallyldimethylammonium) (2⁺). Electrochemical studies of the film formation are reported. The films (50–300 μm thick) were removed from the electrode and characterized by XPS, ESR, UV, VIS, NIR, and IR spectroscopy. The films were stable in dry air for months. They contain 2⁺ and anion radicals (1⁻) in the form of π-dimers and π-stacks. IR spectra showed the optical conduction band at 4 μm and three vibronic bands assigned to π-stacks. Polarized transmission NIR spectra of thin films taken at various incidence angles and ESR spectra on free standing films, which were oriented in the cavity, showed that the stacks were oriented preferentially in the film plane, with a tilt angle of 5° up from the surface. The electrical conductivity was electronic and highly anisotropic. Measured at ca. 90% relative humidity at room temperature with four probes, in the film plane, $\sigma = 10^{-1}$ S cm⁻¹; across the film plane, $\sigma = 5 \times 10^{-8}$ S cm⁻¹. Measured in dry nitrogen, the in-plane $\sigma = 10^{-4}$ S cm⁻¹. Variable-temperature in-plane conductivity measurements on humidified films showed a linear dependence of σ on T^{-1} over the range 220–300 K and an activation energy of 0.3 eV. There was an unusual minimum in the conductivity at about 180 K. The in-plane conductivity of humidified films also showed unusual temporal dependence, in that, depending on the size of the current step applied, the conductivity improved substantially during the first few minutes of current passage.

We report on conducting polymer films formed from an imide anion radical (1⁻) and a polycation (2⁺). The material is analogous to polymers originally reported by Lupinski and co-workers,[1] who used tetracyanoquinodimethane anion radical (TCNQ⁻) and polymeric polycations like quaternized polyvinylpyridine. This early work was followed by a number of publications[2] which extended the examples and showed that good conductivity (ca. 10⁻² S cm⁻¹) only resulted if both TCNQ and TCNQ⁻ were present in the polymer. It was proposed by analogy with the structure of conducting TCNQ salts that mixed π-stacks of TCNQ and TCNQ⁻ were responsible for the conductivity. Surprisingly, radical anions other than TCNQ⁻ seem not to have been utilized

in this manner with polymeric polycations to form free-standing conducting films.

Important background information concerning 1⁻ has been reported. It has been shown[3] in aqueous media that 1⁻ forms π-dimers and aggregates into π-stacks. These species absorb light in the near-infrared (NIR) region, and it has been possible to determine the λ_{max} of the π-oligomers dimer, through hexamer. Precipitation of 1⁻ as its trisodium salt forms fragile thin films. These films were shown to be anisotropic by ESR. Films which were ground-up and then pressed into pellets were conductive. Both Langmuir–Blodgett (LB) and self-assembled thin films of derivatives of 1 have been reported.[4] Anion radicals could be formed in each layer by electrochemical reduction. The reduced layers did not retain charge on standing in solution and could only be studied using spectroelectrochemistry.

In a preliminary communication[5] we reported that the water-soluble imide 1 could be electrochemically reduced in the presence of a polymeric polycation (2⁺) to precipitate a conducting polymer film. This film was air-stable and anisotropic. Anisotropic conductivity has been reported for a few polymer films,[6] usually after drawing the films to orient the stacks. Anisotropic conductivity has also been reported for ultrathin surface-oriented Langmuir Blodgett films containing TCNQ⁻.[7]

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Because air-stable p-doped conducting polymers, anisotropic conductors, and the electroprecipitation method of preparation are all unusual, we have developed the method and studied the polymer in more detail. In doing so we have applied optical and magnetic resonance analyses of anisotropic structure which are unusual for this field.

Results and Discussion

Described first is a useful method for preparing free-standing films and data on the film composition. Next, we report conductivity measurements, which reveal unusual anisotropy, unusual temperature dependence, and unusual temporal dependence. All of these phenomena are dependent on the hydration of the samples. This discussion is followed by spectroscopic studies which confirm the molecular composition and suggest a structural reason for the anisotropy in conductivity.

Conducting Polymer Preparation and Composition. Previous examples of TCNQ⁻ π-stack/polycation conducting polymers were prepared by precipitation or film-casting methods.[1,2] This was not useful for 1⁻/2⁺. Evaporation of water from aqueous mixtures of 1⁻ and 2⁺ precipitated nonuniform thin films on the walls of the container, which could only be reclaimed as fragile fragments. Because we had experience with the electrochemical method of growing conducting polymers of the polypyrrole, polythiophene type, specifically an analogous composite polymer, poly(*N*-methylpyrrole)/poly(styrenesulfonate),[8] we tried this approach for the desired composite π-stack polymer.

Initial studies utilized a platinum electrode in an aqueous solution of 1 mM **1** and 0.1 M **2**⁺Cl⁻. As previously described,[5] reduction at –0.2 V vs SCE (ca. 10 μA cm⁻²) lead to the formation of a shiny black film on the electrode. After being dried, this film could be peeled from the electrode in pieces about 1 cm² in area and up to 50 μm thick. Films were also obtained using other solid electrodes such as gold, nickel, glassy carbon, and graphite. In other experiments methanol solvent replaced water as a medium for film growth. These films proved to be less soluble in water. In all these cases the film properties were qualitatively similar to those described below.

Electroprecipitation is one of the most valuable methods for the preparation of single-crystal organic conductors which contain π-stacks.[9] To our knowledge the co-electroprecipitation of stacks and a polymeric polycation has not been reported. We hypothesize that it is successful, because the stacks form in solution. Indeed, we have found one case involving a derivative of **1** which only dimerizes (no stacks) in solution and only forms dimers in the electroprecitated polymer.[11] Considering the unusual properties of the polymer reported below, this electrochemical approach seems potentially valuable.

These preparatory scale experiments were supplemented with studies of the reduction of **1** using cyclic voltammetry. It has been previously reported that, in DMF or aqueous tetramethylammonium fluoroborate, **1** gives two reversible couples, corresponding to the formation of anion radical and dianion.[3] The
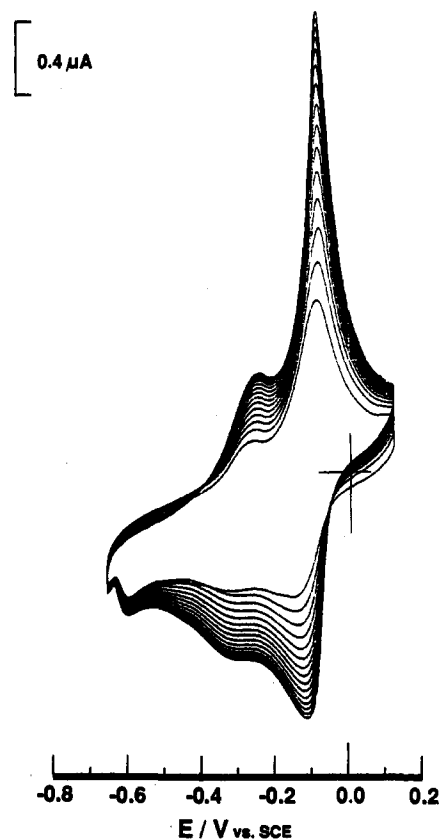
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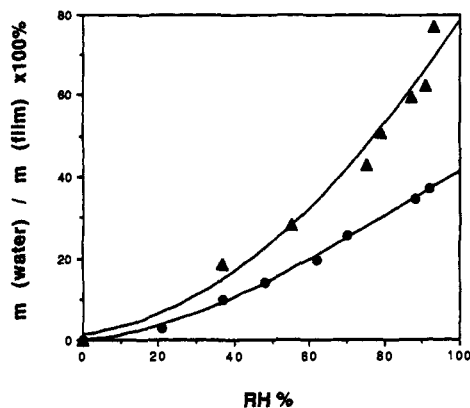(11) Unpublished work of C. J. Zhong.

Figure 1. Cyclic voltammograms on a glassy carbon electrode (0.031 cm²) in 1.15 × 10⁻³ M **1** and 0.35 M **2**⁺/Cl⁻. Scan rate: 5 mV/s.

polymer **2**⁺ was shown to be electroinactive. The voltammogram of aqueous solutions of **1** with **2**⁺Cl⁻ (Figure 1) shows reduction at a potential 0.3 V more positive than that found in the absence of the polycation. This voltammogram shows a cathodic peak at –0.11 V due to reduction of **1** and an anodic peak at –0.09 V corresponding to its reoxidation as well as other peaks at more negative potentials. On repetitive cycles (Figure 1) the currents increase and the anodic peak becomes sharper. This is interpreted to mean that a redox active film containing 1⁻ is being cathodically deposited on the surface. The sharp anodic peak indicates oxidative stripping of the film from the electrode.

A satisfactory method for the preparation of useful free-standing films utilized a mercury-pool electrode in a three-compartment cell. The use of a liquid cathode allowed easy removal of the film from the electrode without damage. Mercury was not retained on the polymer (see below). The pool was 40 cm² in area, the anolyte was 0.1 M NaCl, the reference was SCE, and the catholyte was a 0.3 M aqueous solution of **2**⁺Cl⁻ containing 2mM **1**. Reduction at –0.3 V (steady currents of ca. 1 μA cm²) gave shiny films with thickness controlled by the time of electrolysis. The film was washed with deoxygenated water, dried with a nitrogen stream, and then lifted off the mercury surface with tweezers and stored between glass plates. A 240-h reduction gave a film which after drying was 200 μm thick.

It was found that concentrations of **1** in the range 10⁻⁴–10⁻² M all led to film formation. The steady currents were larger for higher concentrations, but the film properties did not vary substantially. Concentrations of **2**⁺ greater than 0.1 M were desirable to get precipitation of the film. Lower temperatures also promoted precipitation and gave somewhat more anisotropic films. Therefore, all of the films described below were grown at 4 °C using 1.6 mM **1** and 0.25 M **2**⁺.

Using this method free-standing films were repetitively obtained which had an area of 40 cm² and a wet thickness of up to 1 mm. When the film was removed from the electrode and solvent, it quickly dried in the laboratory atmosphere. Upon drying it became stiff, and shrinkage led to ruffling of the surface and

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Figure 2. Humidity dependence of water absorption for a 1⁻/2⁺ film (filled circles) and a 2⁺/Cl⁻ film (filled triangles). m(water) = mass of water, m(film) = mass of dry film.

occasionally some cracks in the film. When wet, the film surface was sticky; when dry, it was hard. Gravimetric experiments demonstrated that the film reversibly hydrated in humid nitrogen. The weight at 90% relative humidity was 40% larger than that in dry nitrogen (Figure 2). This increase is comparable to that observed for 2⁺ as its chloride salt (Figure 2).

These films were stable in their appearance and conductivity for many months when stored in dry air. Because the films contained anion radicals (1⁻), which are known to react with oxygen in solution, this was initially quite surprising. The stability seems to result because the stacks are more stable than the monomeric 1⁻ species (more positive redox potential) and because surface oxidation does not readily penetrate the solid. These films could be dissolved in water and, indeed, if the film was contacted with a drop of water in the air, decomposition of the film at that spot, producing oxidized 1, was observed. The films were not soluble in a 0.1 M aqueous solution of 2⁺.

UV–VIS and IR measurements on the free-standing film confirmed the presence of 1⁻ (see below). To investigate the stoichiometry, film samples were carefully dissolved and oxidized in D_2O. The NMR spectra revealed only signals from 1 and 2⁺. Integration of the peaks gave the concentration ratio [2⁺]/[1], where [2⁺] indicates the concentration of repeat units of poly-cation. It was determined that this ratio depended on the concentration of 2⁺ in the solution used to electrochemically deposit the film. The concentrations used to deposit the films for all the studies described below were 1.6 mM 1 and 0.25 M 2⁺. NMR analysis of these films gave [2⁺]/[1] = 7.5 ± 1. When the preparation solution was more concentrated in 2⁺ (0.5 M), [2⁺]/[1] was 14, and using 0.1 M 2⁺, [2⁺]/[1] was 4. Considering the usual film formed from a 0.25 M 2⁺ solution, these results suggest that the films should contain chloride ions (from 2⁺Cl⁻) to balance the charge, e.g. a composition of 1⁻/7.52⁺/4.5Cl⁻. XPS and combustion analyses gave results in approximate agreement with this composition. However, because the films are hydrated, because we showed that chloride can be exchanged out of film by water washing, because XPS only analyzes the surface, and because combustion analyses on aromatic imides have been found to usually result in incomplete combustion (low %C), the absolute value of these elemental analyses (Experimental Section) is doubtful. Indeed, that is the reason for employing the NMR analysis.

Conductivity Measurements. Consider first the four probe measurements of the conductivity along the film plane (σ_p) made at 90% relative humidity. Although a standard four-point-probe apparatus gave similar results, all the reported measurements were made on samples which had four wires attached in a line, as described in the Experimental Section. Because of the temporal dependence (see below), measurements were made after a few minutes of current passage, when steady values were apparent. Under these conditions the resistances were ohmic; i.e., there was a linear dependence of the measured voltage on the applied current.

Nineteen samples were studied which had dry film thicknesses from 50 to 200 μm. Using a 10 MΩ voltmeter, the room temperature σ_p = 0.2 S cm⁻¹ (SD 0.3). Passage of sufficient charge through the film to electrolyze most of the ions did not result in any increase in the resistance. We conclude, therefore, that the conductivity is primarily electronic. There is no depletion of the conducting entities due to electrolysis.

Consider next a comparison of σ_p with the conductivity across the film plane (σ_a). Because the films were thin, it was not possible to make four-point measurements across the film. Instead, two-point measurements were made using either attached wires (apparent σ_a = 10⁻⁷ S cm⁻¹) or a mercury drop/film/metal contact sandwich (apparent σ_a = 10⁻⁶ S cm⁻¹). *This demonstrates that the ratio of conductivity along the film plane and across it is greater than 10^5 S cm⁻¹.*

The difference between σ_p and the apparent σ_a is rather large, and it was of importance to determine the contribution of the contact resistance to these measurements. In order to achieve a more accurate value for the small σ_a, a device with 1-GΩ impedance was employed. Two- and four-point-probe measurements were made along the film plane, which could be compared with two-point measurements of σ_a. It was assumed that the contact resistance should be the same for measurements across or parallel to the film and could be evaluated by comparing the two- and four-point measurements parallel to the film. This value for the contact resistance was then subtracted from the measured resistance across the film, allowing calculation of σ_a = 5 × 10⁻⁸ S cm⁻¹. Thus, it is clear that the film is semiconducting along the film plane but insulating across the film.

Although the value of σ_a remained constantly low as the humidity above the sample changed, σ_p varied substantially. As previously reported, σ_p for a 50-μm film dropped to 7 × 10⁻³ S cm⁻¹ at 10% relative humidity. In dry nitrogen the value dropped to about 3 × 10⁻⁴ S cm⁻¹. Since σ_p has been established to be electronic, the water effect is of some interest. Absorption of water swells the film and noticeably plasticizes it. This however, does not provide an obvious explanation of the increased conductivity. Indeed, dilution of the film could lower the electronic conductivity.[10]

Temperature dependence of σ_p was measured with a commercial cryostat over the range 110–300 K. In order to get reproducible hydration of the sample over long periods of time, the sample, at 90% humidity, with its four wire probes in place, was sealed in silicone rubber or epoxy. It was recognized that this protective coating might somewhat dehydrate the film during preparation, but since the commercial cryostat held the sample in vacuo, it was necessary. This procedure gave a room-temperature σ_p = 3 × 10⁻² S cm⁻¹ reproducibly over a period of months, even through several heating and cooling cycles. In the range 220–300 K the conductivity decreased with decreasing temperature (Figure 3). A plot of σ_p vs T^{-1} led to a value of 0.3 eV for the activation energy, E_a. Thus, in this range of temperature the material behaves as a semiconductor.

Below 220 K the behavior was quite extraordinary. Shown in Figure 3 are resistivity vs T data. The experiment was initiated at low T, giving σ_p = 8 × 10⁻⁷ at 110 K. The conductivity increased slightly with increasing temperature up to about 160 K. It then dropped rapidly to a minimum of about 10⁻⁷ S cm⁻¹ at about 170 K and then increased again. A careful analysis shows that the change is more rapid between 170 and 220 K than above 220 K, where the E_a = 0.3 eV semiconductor behavior sets in, so that it appears that there is a true valley in the conductivity. The temperature and magnitude of this minimum in the conductivity varied somewhat from sample to sample (perhaps because of variations in hydration), but it was always observed. One explanation is that a change in morphology occurs near 170 K, and at the transition temperature the conductivity is somewhat smaller than that for either the high- or low-temperature structures.

Finally, it is of interest to report the unusual voltage/time transients (Figure 4) that are observed when current is applied
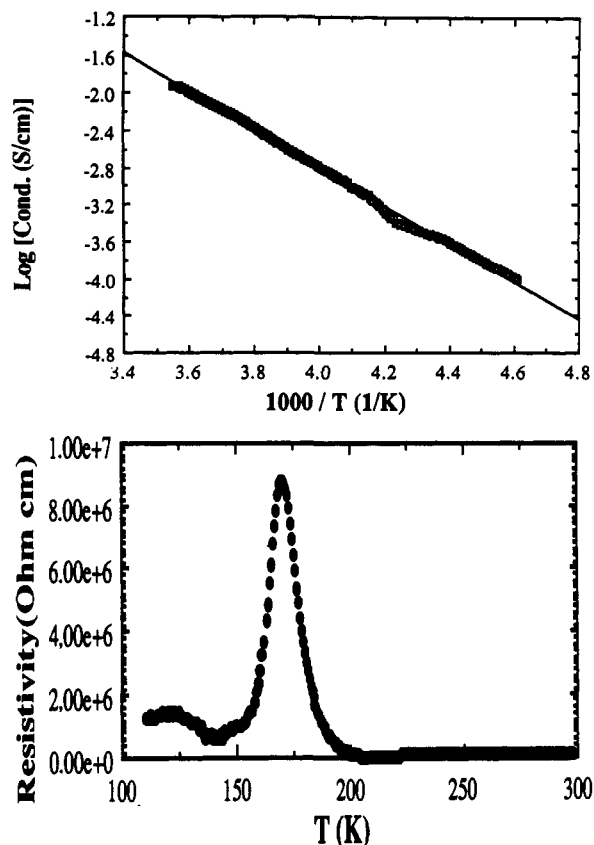
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Figure 3. Temperature dependence of conductivity (above) and resistivity (below) obtained with a $1^-/2^+$ film sealed with epoxy at relative humidity 80%. $I = 5 \times 10^{-3}$ μA (below) and 10 μA (above).

in the four-point-probe configuration along the film plane of hydrated samples. For clarity we have arbitrarily defined positive and negative currents and voltages. For example, a positive 10-μA current applied as a step to the outside electrodes gave an initially large positive voltage across the inside electrodes, which decreased by about 80% to a nearly steady-state value over a period of a few minutes. This shows that the material is becoming more conductive with time.

When the applied current was then stepped back to zero, there was a transient negative change in the voltage across the inside electrodes (Figure 4) which mirrored that originally observed. That is, the voltage changed rapidly in the negative direction and then decayed over a period of minutes back to near zero. (There is a small residual voltage on the inside electrodes even after many tens of minutes.) A current step in the negative direction gave an initially high negative voltage and decay, which mirrored that described above for positive currents. Maximum values of the voltage were measured just after current steps, and both maximum and steady-state values followed Ohm's law (Figure 4).

These changes in conductivity are less than a factor of 10, and a detailed investigation and explanation of the transients was beyond the scope of this investigation. However, we put forward the hypothesis that they arise from polarization of the sample due to migration of ions in response to the applied field. Classically, polarization is suggested when increasing voltages are measured following a current step in a two-electrode conductivity measurement. We have measured such voltage increases on these samples and note that in the four-probe measurement the time scale of decreasing voltages on the inner electrodes and increasing voltages on the outer electrodes is the same. It is reasonable that the hydrated samples would allow some ion migration, and indeed, there are some small ions (dimers) present (see below). A future publication will treat this phenomenon more carefully, but it is worth noting that if "polarization" involves oxidation and reduction of the 1^- aggregates, the behavior can be understood following Wilbourn and
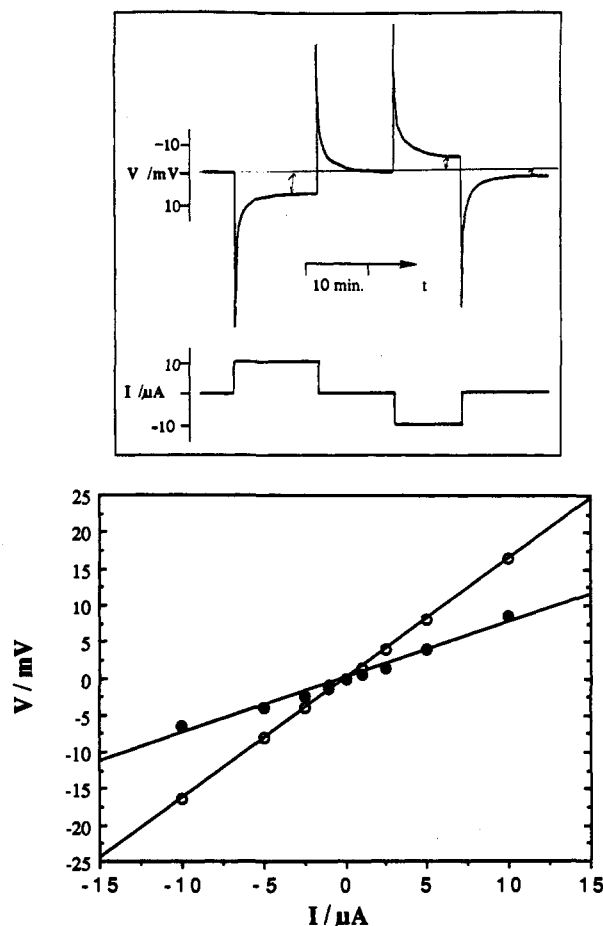

Figure 4. (Above): Transient behavior of voltage measured upon applying current for a $1^-/2^+$ film at relative humidity 80%. (Below): Voltage-current curves. Open circles correspond to the initial voltage, and the filled circles to the stable voltage.

Murray,[10] who studied polarization of solvated films of a conductive ladder polymer.

Optical Spectroscopy. Spectra were recorded over the wavelength range 300 nm to 10 μm. By using this broad range of wavelengths it was possible to sample $\pi-\pi^*$ bands, so called optical conduction bands and vibrational bands. Previous studies of **1** and **1**⁻ in solution provided models for understanding the structure.[3] The VIS-NIR spectra (Figure 5) were recorded in the transmission mode for thin films of the polymer which had been grown on optically transparent tin oxide (ITO) electrodes. It is recognized that these thin films may not be representative of thicker films, especially because of surface oxidation. Even so the method is quite powerful, Studied in air, the film showed bands at 370 and 437 nm and a rising absorption beginning near 1200 nm in the NIR. Transmission IR spectra (Figure 6) on free-standing films show that this NIR band maximizes at 4.0 μm.

It is proposed that this NIR-IR electronic transition is due to π-stacks. It has been shown[3] that 1^- forms π-dimers and π-stacks in aqueous media, and it is known that 1,4,5,8-naphthalenetetracarboxylic acid anhydride anion radical, like many other ion radicals, is stacked in the solid.[20] In solution it has been demonstrated that the π-dimer absorbs at 1140 nm, with larger aggregates absorbing at consecutively longer wavelengths, i.e., pentamer at 1850 nm.[11] Solid molecular conductors show this type of NIR or IR absorption.[12] In π-stacked materials it is excitonic, is polarized along the intermolecular stack axis, and is called the optical conduction band. In dimers the band is called a charge-transfer (CT) band, and it is polarized in the same direction, along the intermolecular axis. Thus, the polymer $1^-/2^+$

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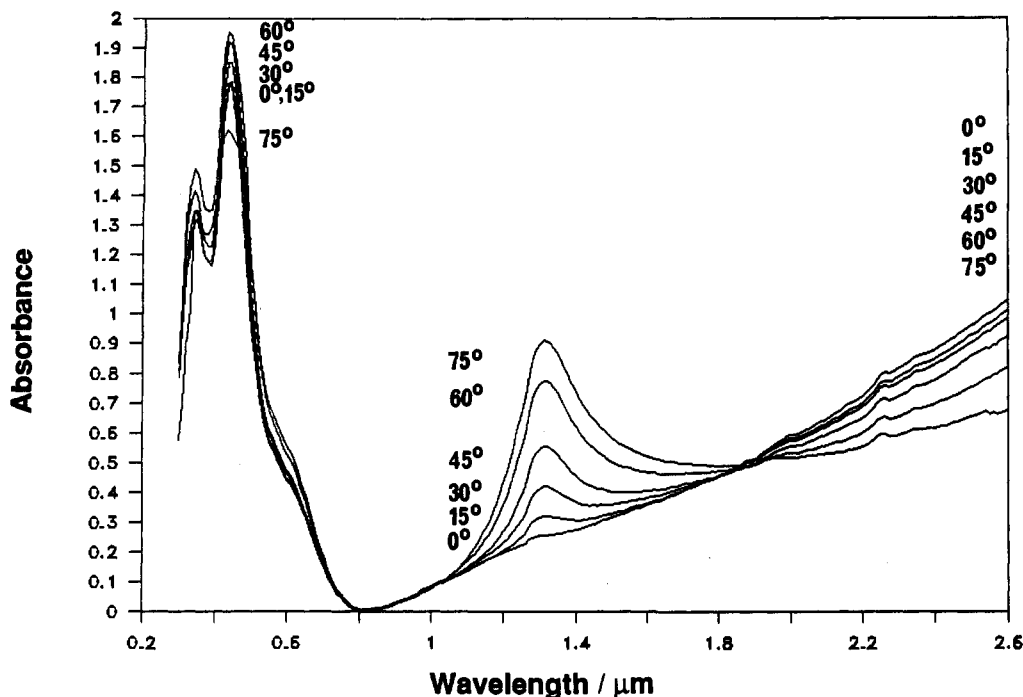
Figure 5. Angular (γ) dependence of the polarized transmission Vis–NIR absorbance of a $1^-/2^+$ film/ITO plate. $\gamma = 0°$ corresponds to the E vector in the film plane.

contains short π-stacks absorbing in the NIR and long π-stacks absorbing in the IR.

The VIS band at 437 nm is assigned to a π–π^* transition of the anion radical as part of a π-stack. Solution studies[3,11] have shown that monomeric 1^- (DMF solution) absorbs at 480 nm, dimeric 1^- (in water) absorbs at 451 nm, and π-stacked 1^- (in aqueous NaCl or in the presence of low concentrations of 2^+ in water) absorbs at 439 nm. Thus, $1^-/2^+$ (437 nm) contains mainly π-stacks. The band at 370 nm is assigned to neutral 1 present in (or on) the film. The intensity of this band was substantially reduced when the sample was handled under argon. This suggests that surface oxidation of the film was responsible for the detection of neutral 1. The thinness of the films on ITO necessarily emphasizes the relative amount of surface contamination compared to that of thicker, free-standing films.

These data confirm the molecular structure and are in agreement with the idea that the conduction involves π-stacks of anion radicals. It is an open question if the stacks contain some dianions or neutrals to achieve mixed valence (as in TCNQ/TCNQ$^-$). It has been shown that neutral 1 does not enter stacks of 1^- in solution,[11] but dianions might do so. The VIS spectra demonstrate that there are no monomeric dianions present in the film, and formed at –0.2 V, few dianions should be present.

It was expected from the conductivity data that the film would be anisotropic. This was investigated in the VIS–NIR using polarized transmission spectra at varying incidence angles. The orientation is defined such that the electric vector of the polarized incident beam is parallel to the $(x-y)$ film plane at $\gamma = 0°$ and perpendicular to the film plane at $\gamma = 90°$. Tilting the film affects the angular relationship of the electric vector of the light and the dipole vector of the transition, and therefore, the intensity of the absorption band.[13] As an example, consider a transition that has its dipole vector aligned parallel to the film plane. The absorption band will have maximum intensity when the incident light is perpendicular to the film plane ($\gamma = 0°$). Shown in Figure 5 are spectra taken through ITO at several incident angles. Qualitatively, it can be seen that the NIR exciton absorbance, i.e. at 2600 nm, and π–π^* absorbance at 437 nm decrease in intensity as γ increases. In contrast, absorption at 1200 nm dramatically increases as γ increases, revealing a narrow band

at 1150 nm. This band is assigned to the CT transition of the π-dimer.[3,11] Keeping in mind that the optical path length through the sample increases as γ increases, it is clear that the dipole vectors of the long π-stacks samples at 2600 nm are oriented more or less along the film plane, while the dipole vector of the dimer CT band is oriented more or less perpendicular to the surface.

A quantitative treatment of the data allows calculation of the tilt angle of the stacks and the dimers relative to the surface. Consider Figure 7, where γ is the angle between the $x-y$ film plane and the electric vector E of the polarized incident light, θ is the angle between the $x-y$ film plane and the dipole vector of the transition of interest, and β is the angle between the y-axis and the projection of the transition dipole vector on the $x-y$ plane.

The transition moment (μ) can be written as

$$\mu = \mu_x \mathbf{x} + \mu_y \mathbf{y} + \mu_z \mathbf{z}$$

with

$$\mu_x = \mu \cos \theta \sin \beta$$

$$\mu_y = \mu \cos \theta \cos \beta$$

$$\mu_z = \mu \sin \theta$$

The electric vector (E) of the polarized light has the following form

$$\mathbf{E} = E_x \mathbf{x}' + E_y \mathbf{y}' + E_z \mathbf{z}'$$

with

$$E_x = 0$$

$$E_y = E \cos \gamma$$

$$E_z = E \sin \gamma$$

The absorbance, A, is proportional to the square of a scalar product of μ and E (k is a constant)

$$A = k|\mu \cdot \mathbf{E}|^2$$
$$= k(\mu E)^2 (\cos \theta \cos \beta \cos \gamma + \sin \theta \sin \gamma)^2$$
$$= k(\mu E)^2 \left(\frac{\sqrt{2}}{2} \cos \theta \cos \gamma + \sin \theta \sin \gamma\right)^2$$

Since the experimental spectra were unchanged when the film was rotated in the $x-y$ plane, the transition moments are isotropic

(13) Michl, J.; Thurlstrup, E. W. *Spectroscopy With Polarized Light*; VCH Publishers: Deerfield Beach, FL, 1986.
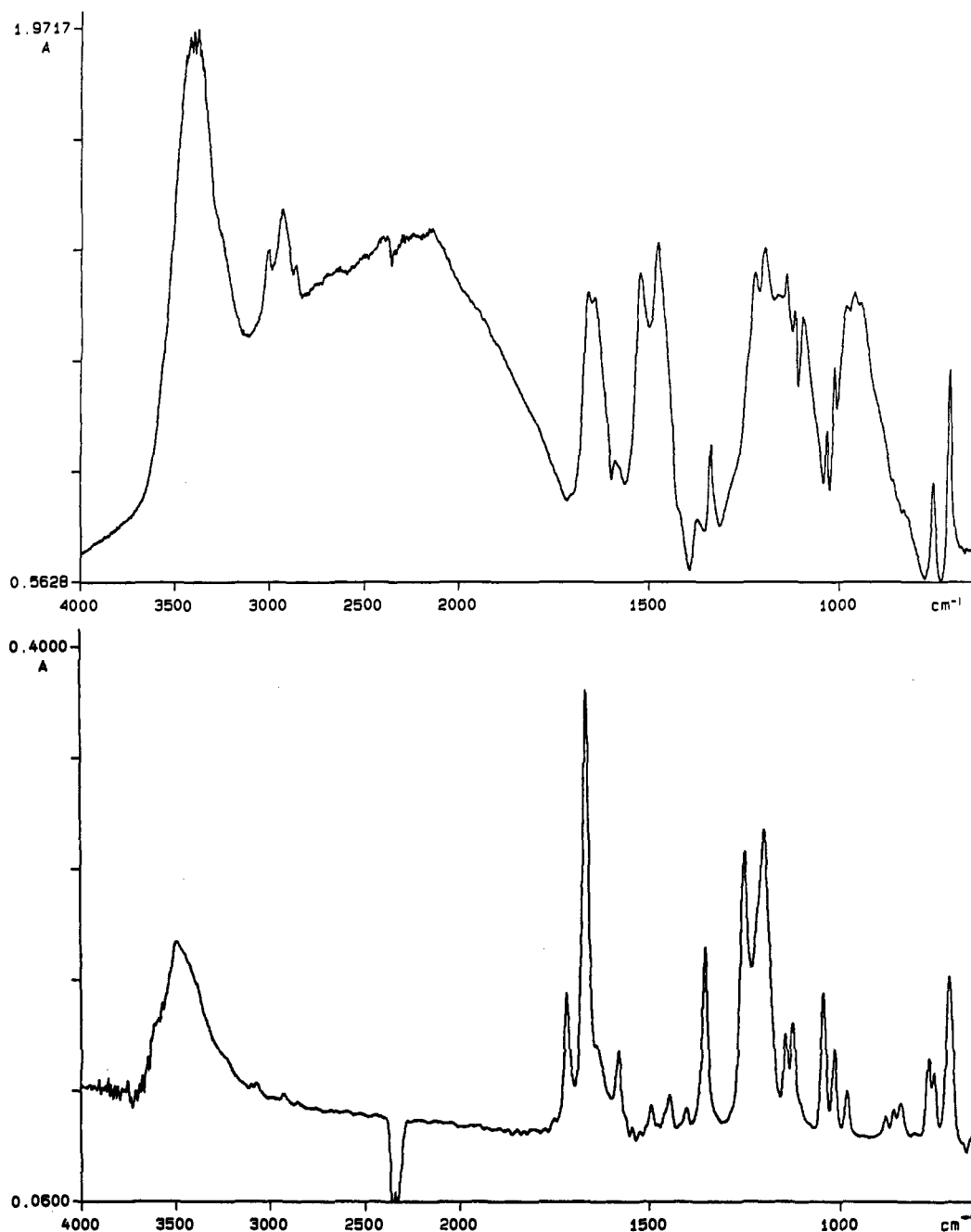
Figure 6. Transmission FTIR spectra of a free-standing 1⁻/2⁺ film (above) and a KBr pellet of 1 (below).
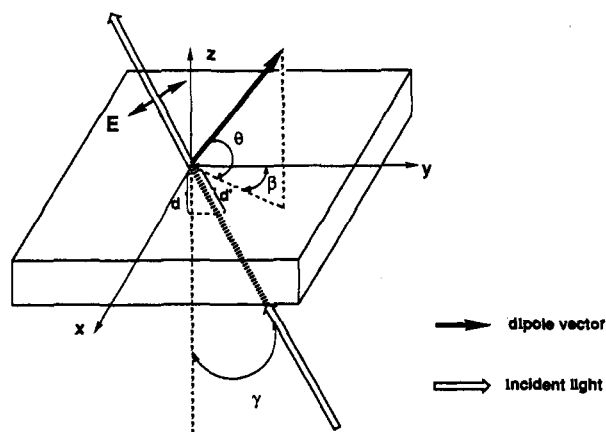

Figure 7. Geometric description of the dipole vector in a film: incident light vector, E vector, and their relationship.

in the film plane and $\beta \approx 45°$. Taking $k(\mu E)^2 = k'$ and taking account that the path length through the film depends on ($1/\cos$

γ) (Figure 8), the working equation is

$$A = k'(\cos \gamma)^{-1}\left(\frac{\sqrt{2}}{2}\cos \theta \cos \gamma + \sin \theta \sin \gamma\right)^2 \quad (1)$$

The validity of this equation was checked by calculation of working curves for dipole vectors with $\theta = 0°$, $54.7°$ (an isotropic film), and $90°$. As shown for $\theta = 0°$ in Figure 8, the maximum absorbances occurred at $\gamma = 0°$, $45°$, and $90°$, respectively, as expected.

The experimental data normalized for comparison with theory are shown in Figure 8. The 2600-nm data can be closely fitted to the theoretical curve for $\theta = 5°$. The excitons are polarized along the stack axis, and *it is concluded that the average long π-stack lies tilted only 5° above the film plane.* This correlates well with the ESR data (below) and explains the anisotropic conductivity.

The average π-dimer (which is ESR silent and probably does not contribute to the conductivity) has its CT band tilted 60° up from the film plane (Figure 8). Because the relative geometry of the two 1⁻ units in the dimer is not accurately known (molecules exactly aligned or slipped somewhat), this measurement does not
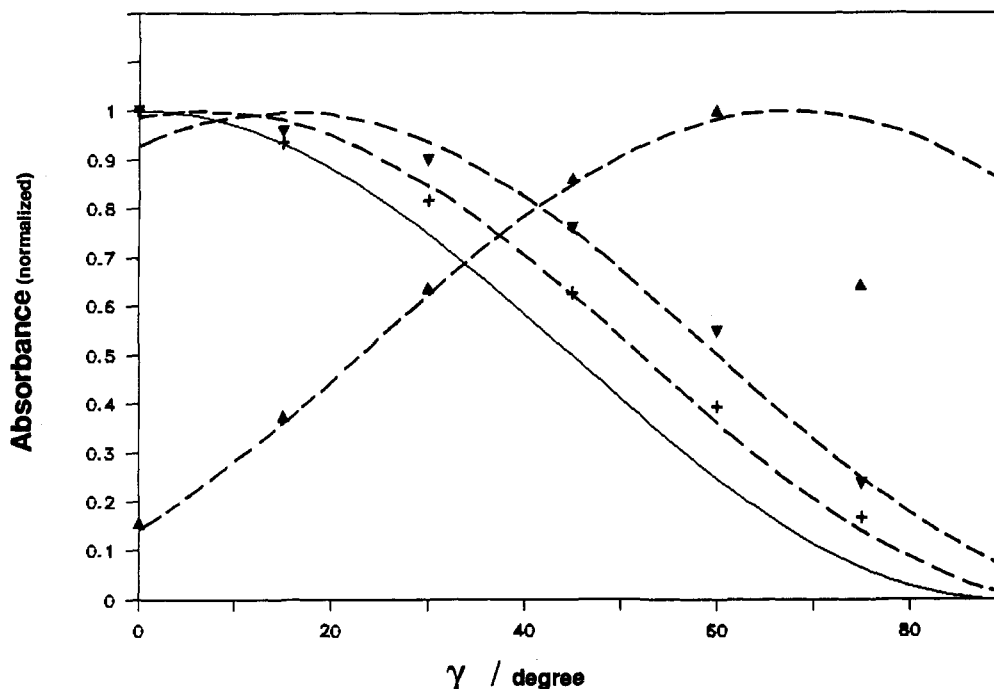
Figure 8. Dependence of absorbance on incident angle of polarized light. The solid line is the theoretical curve for $\theta = 0°$ (eq 1). Experimental data was collected at 1150 nm (▲), 435 nm (▼), and 2600 nm (+). Curves drawn through the points are theoretical for $\theta = 60°$, 11°, and 5°, respectively.
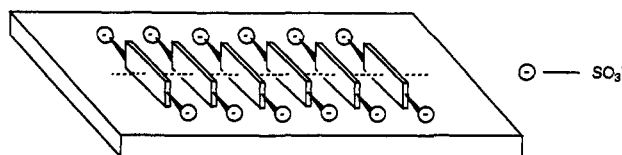

Figure 9. Oriented π-stack of 1⁻.

define the tilt angle of the two molecules in the dimer, but it is likely that the average molecular plane is more or less in the plane of the film. Thus the long axes of both the π-dimers (molecular axis) and long stacks (stack axis) tend to lie in the film plane.

Interpretation of θ for the $\pi-\pi^*$ band must take into account that many different π-aggregates are involved. We assume that at 437 nm the contribution from dimers and very small stacks is small (the dimer should absorb at 451 nm),[11] and we interpret the result in terms of longer stacks. It is known from PPP calculations[11] that the $\pi-\pi^*$ band is polarized along the nitrogen-nitrogen axis of 1⁻. Analysis of the experimental data (Figure 8) shows that the average anion radical in a stack has this axis tilted up from the film plane by 11°. This is consistent with a model in which the average π-stack, which runs along the film plane, is composed from 1⁻ molecules with the nitrogen-nitrogen axis also almost in the film plane (Figure 9). This model can be further refined by consideration of the shift in the $\pi-\pi^*$ band to shorter wavelength as one goes from monomer to stack.[3,11] It is well established from theory[14] and experiments on dye molecules[15] that such blue shifts occur when the $\pi-\pi^*$ transition dipoles of the molecules in the stack are at an angle greater than the magic angle of 54.7° with respect to the stack axis. Shown in Figure 9 are molecules with their nitrogen-nitrogen axis at 90° to the stack axis. The experimental data leave as an open question the orientation of molecules with respect to the short molecular axis.

IR spectra were taken on free-standing films about 10 μm thick (Figure 6). These spectra show absorption from water at 3500 cm⁻¹, CH stretching vibrations near 3000 cm⁻¹, the peak of the optical conduction band near 2200 cm⁻¹, carbonyl vibrations at 1662 and 1645 cm⁻¹, and multiple bands near 1500, 1200,

1100, and 1000 cm⁻¹. Comparison of the spectra of the neutral 1 with that of the polymer shows major differences. In addition to the optical conduction band, there are three sets of new bands at 1500, 1100, and 900 cm⁻¹. It is expected that 1⁻ will have a spectrum only slightly perturbed from that of 1, and following the literature,[16] these bands are assigned to totally symmetric vibrations which are allowed due to coupling to the IR electronic transition. Thus, the IR data are in agreement with the proposed π-stack structure.

ESR Spectra. Small pieces (0.1–0.3 cm²) of free-standing film were placed in an evacuated tube and studied in two orientations: film plane parallel to the applied field (par) or film plane perpendicular to the applied field (perp). X-band spectra taken at room temperature (Figure 10) gave different signals for the two orientations, confirming the structural anisotropy. The perp configuration gave an asymmetric peak broadened on the high-g-value side. The par configuration gave a more symmetrical signal. At 77 K the patterns changed (Figure 10). Now the par configuration was asymmetric, broadened on the low-g-value side, while the perp configuration was more symmetrical. In both cases the perp spectrum was at higher g-value than the par spectrum. Over the temperature range 77–230 K the doubly integrated signal intensity remained constant within 10%. This is expected from a Pauli spin system.[17]

Further details of the orientation of the π-stacks in the 1⁻/2⁺ film were revealed in the ESR spectra obtained with a Q-band (23 GHz) spectrometer (Figure 11). The spectra were observed at room temperature and at 95 K with the magnetic field parallel to and perpendicular to the plane as before. These spectra can be explained and simulated (Figure 11) if it is assumed that there are two types of species present. One is π-stacks which are preferentially oriented parallel to the plane of the film. The other is small stacks that give an isotropic signal (rapid rotation) at room temperature but an anisotropic signal (slow rotation) at 95 K. The spectra were simulated on the basis of the following assumptions: (1) the presence of the oriented stacks and mobile stacks with a 2/1 ratio, (2) g tensors of $g_{\parallel} = 2.0023$ and $g_{\perp} = 2.004\,96$ for both stack types, and (3) that the stack axes in the oriented regime are evenly scattered within the range $\theta = 0$–30°.

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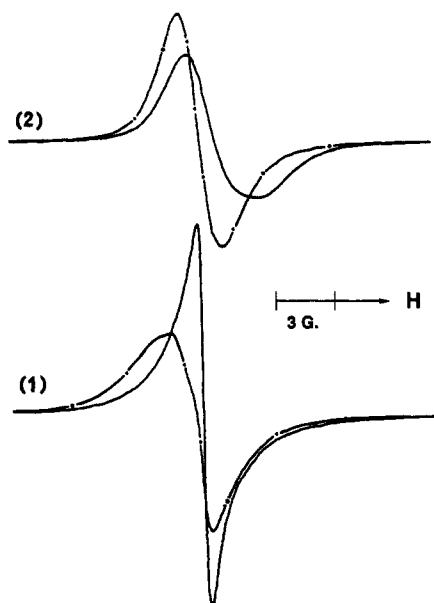
Imide Anion Radical and Polycation Polymer Films

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Figure 10. Orientation dependences of X-band ESR spectra for a free-standing $1^-/2^+$ film at (1) room temperature and (2) 77 K. The film plane is either parallel to the magnetic field H (solid line) or perpendicular to H (solid-dot line).

Assumption 3 is a crude model meant to account for the dispersion in stack direction and the motion of these stacks. Assumption 2 is reasonable in that if the planes of the monomers in the stack are perpendicular to the stack direction, the *g* value in the stack direction is expected to the exactly equal to the free-spin value (2.0023). In the perpendicular direction, the large spin orbit coupling constant of oxygen atoms and their nonbonding lone-pair electrons should cause a positive *g* shift as observed. The success of this simulation qualitatively substantiates the optical analysis which shows long stacks oriented in the film plane.

We have also measured the X-band spectra of these polymer samples in air, where they may be more highly hydrated. The spectra are quite similar. Similar anisotropic properties have been reported for LB films with TCNQ⁻ stacks running parallel to the film plane.[7,18] In contrast to one of these cases[18] (and many CT salts), we find no evidence for triplet (exciton) spectra at any temperature or sample orientation. Finally, we note that although Dysonian line shapes have been found for semiconducting organics, $1^-/2^+$ samples, especially at low temperature, are not sufficiently conducting to give a significant skin effect.

Conclusions and Comparisons

Using co-electroprecipitation of anionic π-stacks and a polymeric polycation, it is possible to prepare an air-stable, n-doped conducting polymer. Free-standing films of considerable size, and thickness up to 300 μm, are prepared using a mercury cathode. These films contain π-dimers and π-stacks of 1^- with the charge balanced by the polycation 2^+. Although electrodeposition is a common method for forming conducting polymers, it has not been used to form π-stack conductors. Of interest is the mechanism of deposition and how it can account for the structural anisotropy. Since it is known that 1^- associates with 2^+ in solution to form π-stacks,[11] we suggest that the mechanism involves precipitation of preformed stacks, which have been formed at the interface of the solution and growing film. This has good analogy in the mechanism for electrocrystallization of conducting charge-transfer salts.[9] On a flat electrode stacks might precipitate with the stack axis parallel to the surface in order to maximize van der Waals forces. Surprisingly, this anisotropic growth continues, eventually providing anisotropic thick films.

The anisotropy in conductivity apparently arises from the orientation of the π-stacks. Although a number of polymers have been formed into anisotropic conductors,[6] the anisotropy in conductivity is usually much smaller ($<10^2$). A material of interest here is a polymer, similar in that it is formed anisotropically and contains stacks. This is tetrathiotetracene formed by zone refining crystals in an inert polymer matrix.[2t] The long axes of the needles run along the high-conductivity axis, giving an anisotropy > 10^3.

High anisotropy has also been measured for LB films containing TCNQ⁻/TCNQ⁰ stacks.[7] An LB film of interest, N-docosylpyridinium TCNQ⁻, contains anisotropic TCNQ π-stacks with ESR *g*-values of 2.0024 along the stack (film) direction and 2.0035 along the short molecular axis.[7a] These values are similar to those for $1^-/2^+$, and the spectra are similar. The σ_p for such LB films are in the range 10^{-2}–10 S cm⁻¹.[7]

A crystalline model for the polymer is (TCNQ)₂methylpyridinium,[19] which has a room-temperature conductivity $\sigma = 2 \times 10^{-3}$ S cm⁻¹, $\Delta E \approx 0.2$ eV, exciton band maximum at 2.5 μm, and three enhanced IR vibronic bands in the range 1550–1100 cm⁻¹. $1^-/2^+$ has $\sigma_p = 0.1$ S cm⁻¹, $\Delta E \approx 0.3$ eV, $\lambda_{max} = 4$ μm, and three vibronic bands in the range 1530–960 cm⁻¹. A less studied but structurally more similar example is a crystalline salt formed from partially reduced 1,4,5,8-naphthalenedicarboxylic acid anhydride.[20] The crystal is formed from mixed-valence stacks (one neutral and four anion radicals). The salt as a pressed powder shows $\sigma = 5 \times 10^{-2}$ S cm⁻¹ at room temperature.

The enhancement of electronic conductivity by hydration which was found here is rare but has been reported for polyaniline.[21] Hydration also leads to important increases in the conductivity of insulating polyimide films.[22] Although 1^- is also an imide, the structure of the two materials is quite dissimilar. In the polyimide case, a humidity sensor has been developed[23] and a similar device can be imagined for thin films of $1^-/2^+$ where the film resistance would be a measure of the humidity. Uses for the anisotropy might also be imagined considering that there is a commercial adhesive tape sold for its quality of conductance across the thin film but not along the tape.

This work expands the field of conducting polymers in terms of preparation method, structure, and properties. The method and similar materials seem worthy of further study.

Experimental Section

Materials. The synthesis of compound **1** has been reported.[3] Poly-(diallyldimethylammonium) chloride was purchased from Polyscience (MW = 240 000) or as a 15% solution from Aldrich Chemical. As previously noted the Aldrich Chemical sample has some olefinic impurity, but both materials gave satisfactory results in the present study. The ITO electrodes were from Delta Technologies, 13960 N, 47nd St., Stillwater, MN (#CH-80IN-1515).

Spectroscopy. The spectrometers have been previously described,[3,4] except for the Q-band ESR spectrometer, which is a Brucker 300 equipped with an EROS 1 Q-band bridge.

Conductivity. Four copper wires of 0.15-mm diameter were attached about 1 mm apart, in a line, to one film surface using silver paste (Ted Pella Inc.). Another wire was attached to the other surface for measurement of σ_a. Small indentations were carved on the surface to ensure a good contact. In the home-made device a constant current was passed between the outer electrodes with an EG&G PARC Model 173 galvanostat. The voltage was measured across the inner electrodes and the conductivity calculated according to $\sigma_p = LI(dWV)^{-1}$, where *L* is the distance between inner electrodes, *I* is the current, *d* is the thickness

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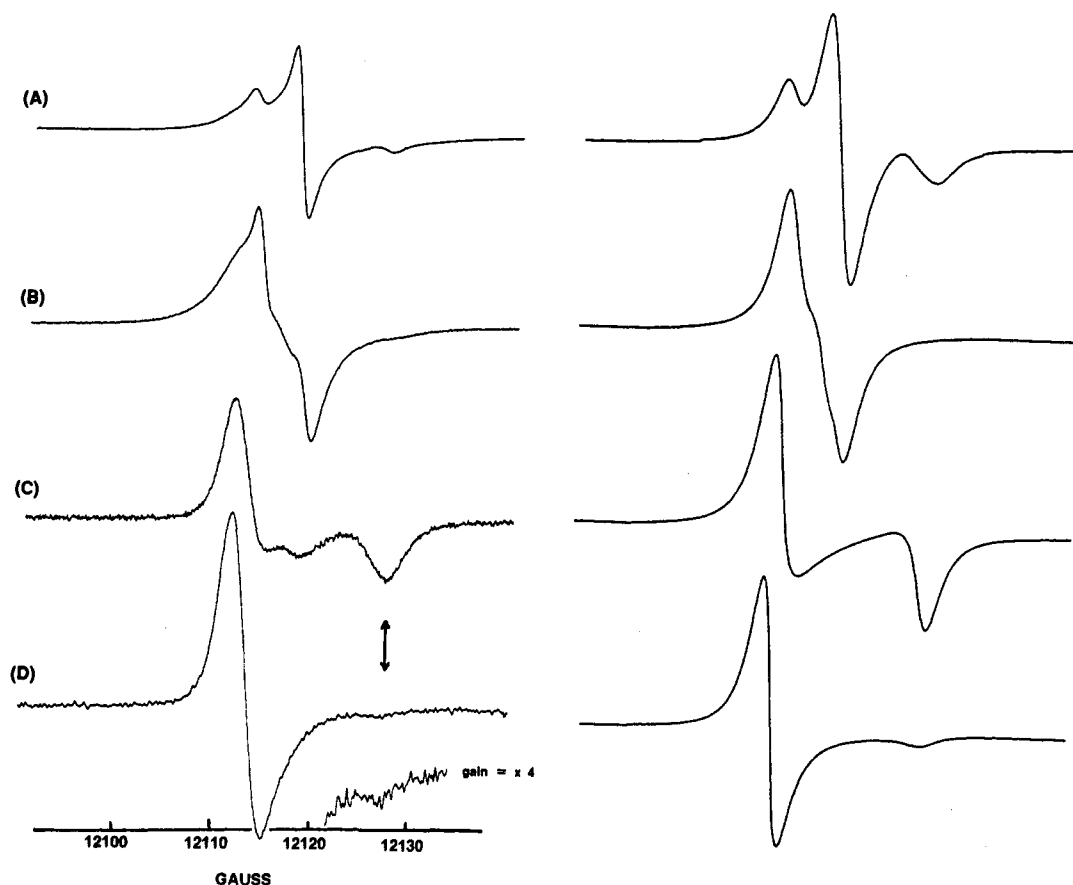(23) Denton, D. D.; Ho, C. N.; He, S.-G. *IEEE Trans. Instrum. Meas.* **1990**, *39*, 508.

Figure 11. Experimental (left) and simulated (right) Q-band ESR spectra for $1^-/2^+$: (A) room temperature, film plane parallel to H; (B) room temperature, film plane perpendicular to H; (C) 77 K, film plane parallel to H; (D) 77 K, film plane perpendicular to H. The arrow marks $g = 2.0023$.

across the film, W is the length of copper wire contacting the surface, and V is the voltage. Variable-temperature measurements were made with a computer-controlled Dupont instrument. The temperature was lowered to ca. 100 K with liquid nitrogen and then allowed to warm up under computer control. Humidity was controlled by placing the sample in a glass chamber into which was flowed humidified nitrogen gas. The relative humidity in the chamber was measured with a hygrometer. For variable-temperature measurements the film with attached wires was coated with a layer of silicone rubber (General Electric) or 5-min epoxy (Devcon Corp.) a few millimeters thick.

$1^-/2^+$. Conventional three-compartment cells were used for the electrochemical preparation. Graphite rod (in $\sim$0.1 M NaCl electrolyte) and saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. All potentials are reported vs SCE. The working electrodes included platinum, gold, nickel, graphite, ITO, and mercury. Pt and Au electrodes with defined surface area were used for cyclic voltammetry. The catholytes for film preparation were aqueous solutions of 1 and 2^+, with concentrations of 0.1$\sim$0.5 M for 2^+ and 1.0$\sim$3.0 mM for 1. The catholyte was deoxygenated before electrolysis by bubbling N_2 through it for at least 2 h. Electrochemistry was performed with an EG&G Parc 173/175/179 potentiostat/programmer/integrator. The electrolysis was controlled at a potential of ca. -0.3 V; a typical current corresponding to this potential was 1–5 $\mu A/cm^2$. About 50 mC cm^{-2} produced 10 μm of dry film.

Thin films for spectroscopic measurements were prepared on Pt, Au, Ni, and ITO plates, either as a coated film or as a free-standing film, which was peeled off the electrode. The coated film was carefully rinsed with water before drying under vacuum. Such thin films looked shiny, and yellowish to brown depending upon thickness. Thick ($>$100 μm) and free-standing films were prepared on a Hg-pool electrode. A cylindrical

cell had the Hg pool (exposed area of 40 cm^2) with an immersed Pt wire for electrical connection and a graphite rod ($\sim$40 cm^2) in a separate compartment (0.1 M NaCl) located above the Hg pool, separated with a fritted glass disc. After the formation of film, the catholyte was sucked out and the film was rinsed with water and lifted up with tweezers before drying under a flowing atmosphere of argon. Films of up to 300 μm dry thickness were thus obtained. The film looked shiny and black. When dry, the film was stable in dry air. Humid air led to reoxidation of the film. The films were stored between two glass plates under N_2.

Combustion analysis was performed on a sample of $1^-/2^+$ which had been dried under vacuum. Found: C, 54.4; Cl, 9.5; H, 8.0; N, 7.0; S, 2.9. Calculated for $1^-/7.52^+/4.5Cl^-$: C, 61.3; Cl, 9.5; H, 8.0; N, 8.0; S, 3.6. Previous experience in this laboratory and elsewhere has demonstrated that aromatic imides, demonstrated by other means to be pure, usually give low carbon analyses. Also, it has not been established that the analyzed sample was completely dehydrated.

XPS spectra were compared with the spectra of pure 1 and 2^+, showing that the polymer $1^-/2^+$ contains nitrogen, carbon, sulfur, chlorine, and oxygen signals at the expected chemical shifts. No mercury was detected. Both aromatic and aliphatic carbon signals were present, and two nitrogen signals appropriate for ammonium and for imide were measured. Depending upon the extent of washing with water, variably small amounts of Na^+ were found. Atomic ratios were quite variable from sample to sample, even on different pieces of the same film.