

Liquid Crystal Perylene Diimide Films Characterized by Electrochemical, Spectroelectrochemical, and Conductivity versus Potential Measurements

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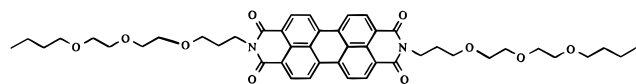
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Electrochemical techniques are used to characterize thin polycrystalline films of a liquid crystal perylene diimide. Cyclic voltammograms show evidence for strong attractive interactions between the perylene diimide molecules and suggest that the film undergoes two structural rearrangements to accommodate reduction to the anionic and dianionic states. Spectroelectrochemical measurements support this interpretation. The redox conductivity of the film as a function of electrochemical potential was measured with the use of interdigitated array electrodes. The conductivity reaches the semiconducting level before the occurrence of the first noticeable reduction wave. The maximum conductivity, 4.4×10^{-2} S/cm, occurs when the film is reduced by 1 equiv of electrons, in contrast to the expectation that this state should be a Mott insulator.

Introduction

Liquid crystalline (LC) derivatives of molecular semiconductors^{1–6} have been developed in an attempt to address some of the limitations of existing materials.^{7,8} One potential advantage of LC semiconductors is that their self-organizing properties may be exploited to grow large area crystalline thin films. Crystallinity improves the electrical characteristics of inorganic semiconductor films but may be especially important for understanding and controlling the properties of the highly anisotropic molecular conductors.^{9,10} Evaporated thin films of typical molecular semiconductors can be crystallized by exposure to solvent vapor or heat, but the process usually destroys the integrity of the film.^{11–13} This results in the loss of electrical contact to the substrate and to other organic layers as well as to electrical short circuits. We considered this a challenge to our ability to rationally design improved variants of organic semiconductors and recently reported the synthesis and preliminary characterization^{5,6} of about a dozen LC perylene diimides. Thin films of one of these, PPMEEM, spontaneously crystallize into highly ordered domains hundreds of microns in length.⁵ Scanning electron micrographs show that these films remain strongly adhered to the substrate.¹⁴ Since PPMEEM is soluble in most solvents, the electrochemical characterization of thin films of a less soluble similar compound, PPEEB, is reported here.



PPEEB

Another major limitation of molecular semiconductors that eventually may be addressed with LC derivatives is their high resistivity. The photocurrents in most organic-based solar cells, even those made with very thin films, show evidence of being

resistance limited at solar light intensities.^{15,16} Even phthalocyanine films that are “doped” with ambient oxygen, making them act slightly p-type, are still quite resistive.¹⁷ Several molecular materials have been doped to metallic proportions,^{18–21} however, so there is no question that it is possible to make these compounds highly conductive. Furthermore, some phthalocyanine derivatives have been discovered with such small band gaps that they are semiconducting even when undoped.²² Still, the range between the insulating state of most intrinsic molecular compounds and their “molecular metal” state remains largely unexplored. Somewhere in this range should lie the semiconducting properties that are most useful for a number of applications. We do not directly address the doping problem here but employ a high-resolution method for measuring the conductivity of molecular films as a function of their effective doping level and show that the conductivity of a PPEEB film can be increased by 10 orders of magnitude through electrochemical doping.

Liquid crystalline semiconductors have been studied for a number of years^{1–4,23–25} and might be expected to exhibit unusual behavior in electrochemical experiments. However, we have found no reports of the electrochemical characterization of such LC thin films. We report here the electrochemical characterization of PPEEB thin films with emphasis on the structural rearrangements and changes in optical absorbance and conductivity that occur as a function of electrochemical potential.

Experimental Section

The PPEEB⁶ films were spin-coated from THF solution onto a variety of substrates. The films ranged from 10 to 100 nm in thickness as determined by the optical absorbance of the films ($\alpha_{469} = 3.2 \mu\text{m}^{-1}$ for the as-spin-coated film before it turns into the black phase^{5,11}) or the optical absorbance of the film washed off opaque substrates into a known amount of chloroform ($\epsilon_{526} = 9.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). The films spontaneously form a polycrystalline array of randomly oriented crystallites similar to that shown in the top half of Figure 2 in ref 5 although the crystallites are only about 3–5 μm in diameter, smaller than

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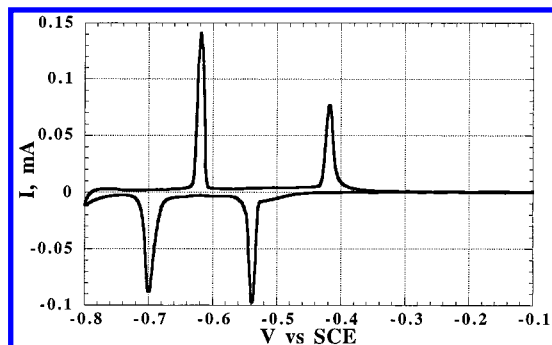


Figure 1. Cyclic voltammogram of a 50 nm PPEEB film ($\Gamma \approx 9.5 \times 10^{-9}$ mol/cm²) on SnO₂-coated glass in 0.1 M LiCl solution. Scan rate 2 mV/s.

those in the PPMEEM films. PPEEB is a solid at room temperature; its LC phase begins at 66 °C.⁶ However, its phase behavior in the presence of aqueous electrolyte or in its reduced forms is not known. The oxidation of the perylene diimide to the cation is not possible in the potential range accessible to aqueous solution, so only the reductions are studied.

The UV-vis-NIR absorption studies employed an HP 8453 spectrophotometer. The spectroelectrochemical measurements were performed in a cuvette with a film of PPEEB on F-doped SnO₂-coated glass (Nippon Sheet Glass) as the working electrode. The cuvette was sealed with a septum and degassed with argon. The spectra of the anion and dianion in solution were obtained with PPMEEM because it is more soluble than PPEEB. Since the optical characteristics are determined by the chromophore, not the side chain, these spectra should be identical to those of PPEEB. An 80 mM solution of degassed aqueous sodium dithionite, Na₂S₂O₄, was added in portions to a 19 μ M solution of PPMEEM in DMF:H₂O (4:1) in a cuvette under flowing argon. The spectra obtained match those reported by Ford et al.²⁶ The reduction potentials of PPMEEM in acetonitrile/LiClO₄ were likewise measured as a surrogate for the less soluble PPEEB.

All experiments on thin films reported here employed N₂-degassed aqueous solutions of 0.1 M LiCl in a single-compartment cell with a platinum counter electrode. Potentials were measured vs an SCE reference electrode except in the spectroelectrochemical experiments that employed a silver wire quasi-reference electrode. The data from a PAR 173/176 potentiostat/controller were digitized with a Macintosh IICI running LabVIEW 4.0. A Pine AFCBP1 bipotentiostat was used for the conductivity measurements at a scan rate of 0.63 mV/s (set to 0.5 mV/s). The data from the bipotentiostat were plotted on a Soltec *x-y-y'* recorder and digitized using Digimatic 2.0. By adjusting the current sensitivity of both potentiostat and recorder "on the fly", the current could be accurately measured over a range of 6 orders of magnitude. The gold interdigitated electrodes (Abtech Scientific) consisted of 50 fingers, 8.5 μ m wide, on each array separated by 11.5 μ m gaps.

Results and Discussion

Electrochemistry of PPEEB Films. A cyclic voltammetric (CV) scan at 2 mV/s of a 50 nm film of PPEEB on SnO₂-coated glass in 0.1 M LiCl solution (Figure 1) shows two sharp, narrow reduction peaks corresponding to the reduction to the monoanion at -0.54 V vs SCE (peak half-width = 8 mV) and to the dianion at -0.70 V (half-width = 16 mV). The conjugate reoxidation peaks are also unusually narrow and occur at substantially more positive potentials than the reductions. Coulometry shows that each peak corresponds to the transfer

of approximately one electron per PPEEB molecule: the charge under each peak, in nmol/cm², is 9.5 and 9.5 for the first and second reductions, respectively, and 10.1 and 8.7 for the second and first reoxidations, respectively. Reversal of the reductive scan at -0.6 V, immediately after the first reduction wave, does not change the shape or potential of the reoxidation peak at -0.42 V. A reproducible prewave (~ -0.45 to -0.52 V) occurring before the first sharp reduction peak accounts for $\sim 15\%$ of the charge of the first reduction. If the scan is reversed at -0.52 V after most of the prewave but before the first sharp reduction peak, a reoxidation corresponding to the prewave occurs with little or no potential shift and the sharp reoxidation peak at -0.42 V disappears. The cyclic voltammetry of the PPEEB films was essentially identical on all substrates tested: ITO, SnO₂, glassy carbon, and interdigitated gold electrodes.

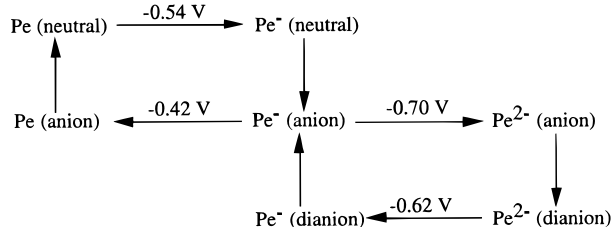
Cyclic voltammetry (not shown) of the more soluble LC perylene diimide derivative, PPMEEM, in acetonitrile/LiClO₄ shows that the reductions to the anion and dianion in solution occur as two closely spaced peaks at -0.42 and -0.52 V, respectively. A non-liquid-crystalline perylene diimide studied in methylene chloride solution showed these reduction waves at -0.73 and -0.96 V.²⁶

Films of surface-confined, noninteracting electroactive species are expected to show cyclic voltammetric peak half-widths at room temperature of 90.6 mV.^{27,28} To observe such behavior, the scan rate must be sufficiently slow that ionic and electronic charge transfers through the film are not rate limiting. Films of most compounds show somewhat broader peaks that may be caused by repulsive interactions between the species or by a distribution of potentials at different sites in inhomogeneous films.²⁹

Peaks narrower than the theoretically expected 90.6 mV also have been observed. Bard and others have explained this behavior as resulting from attractive interactions between the electroactive species,²⁷⁻³⁰ and we interpret our results similarly. The mechanism of the attractive interactions in the case of PPEEB films is not known; however, strong intermolecular interactions are commonly observed in perylene diimide films and are responsible for such phenomena as the intermolecular charge-transfer absorption band^{11,31} and the long-range energy-transfer process.^{12,13} The peaks in the CVs of PPEEB films become broader and the peak splitting increases as the scan rate is increased. For the 50 nm film shown in Figure 1, the peaks begin to take on the shape of diffusion-controlled waves at scan rates around 25–50 mV/s. The appearance of diffusion-controlled behavior begins at slower scan rates when the electrolyte contains larger cations, such as potassium in place of lithium. This suggests that the rate-limiting electrochemical step involves counterion motion through the LC film.

The large potential shift between conjugate reduction and reoxidation peaks observed in PPEEB films is similar to that occurring in films of tetrathiafulvalenium tetracyanoquinodimethane (TTF-TCNQ) and other TTF-containing films.^{30,32,33} Detailed studies of this behavior led to its description by a kinetic "square scheme".^{29,30} In essence, a reorganization or phase change occurs in the film after reduction or oxidation, causing the reverse electron-transfer process to occur at a different potential than the forward process. Applying this interpretation to the cyclic voltammogram of PPEEB (Figure 1) leads to the "double-square scheme" shown in Scheme 1.

We postulate that PPEEB films undergo a structural rearrangement to accommodate their state of reduction. This seems to be a reasonable assumption for films of electroactive liquid crystals, molecules that were specifically designed for their

SCHEME 1: Kinetic "Double-Square Scheme" Proposed To Explain the Cyclic Voltammetric Behavior of the PPEEB Film^a


^a The average charge on the perylene diimide moiety is indicated as a superscript while the term in parentheses denotes the structural form of the film. Horizontal arrows indicate electron-transfer processes, and vertical arrows indicate structural rearrangements.

ability to spontaneously self-organize. However, since there are apparently no electrochemical studies of comparable LC systems, we do not know whether this postulate is generally valid. With this assumption, Scheme 1 interprets the cyclic voltammogram shown in Figure 1 as follows: The neutral PPEEB film, in a structure appropriate to the neutral species, is reduced to the anion at -0.54 V. The film then undergoes a structural rearrangement to accommodate the negative charge on the perylene diimide ring and the accompanying counterion and possible solvent molecules. This rearrangement stabilizes the reduced species; therefore, a more positive potential (-0.42 V) must be applied to the film to reoxidize it back to the neutral form. After reoxidation, the film undergoes the reverse structural rearrangement back to the form appropriate to the neutral species. This describes the first "square" of the double-square scheme shown in Scheme 1. The second reduction and reoxidation are explained similarly. The electrochemical behavior does not change over dozens of cyclic voltammetric scans and is reproducible from film to film. The first scan on a fresh film, however, is different: the first reduction peak occurs at more positive potentials, and the prewave is sometimes observed as a separate peak. This behavior may be caused by the incorporation of electrolyte ions and possibly solvent molecules into the film when it is first reduced.

The initial reduction of the PPEEB film by ~ 0.15 equiv that occurs in the prewave (Figure 1) is electrochemically reversible and does not lead to a rearrangement of the film structure. The percentage of the total charge that occurs in this prewave is largely independent of scan rate. Only when the film is reduced past the prewave does the rearrangement occur. The electrochemistry of the prewave is not included in Scheme 1.

Spectroelectrochemistry of PPEEB Films. The changes in the PPEEB films upon electroreduction were also characterized by spectroelectrochemical measurements. Figure 2 shows the absorption spectra taken at the indicated potentials during the reduction to the anion. The spectrum of the anion dissolved in solution (DMF:H₂O, 4:1) is shown for comparison. (The absorbance around 551 nm is from a small amount of dianion.) Before electrochemical cycling the polycrystalline PPEEB film is black, with an absorption spectrum (not shown) typical of strongly interacting perylene diimide chromophores.⁵ After the first electrochemical cycle, and for all subsequent cycles, the film is red in the neutral state at 0.0 V (spectrum "a", Figure 2). The crystallinity of the film observed under a microscope appears unchanged by this black to red transition. A similar red spectrum is obtained by exposing black films of PPMEEM to warm water vapor, which causes the film to expand, or by spin-coating either PPMEEM or PPEEB from a solution containing LiClO₄.¹⁴ Therefore, we interpret the red spectrum

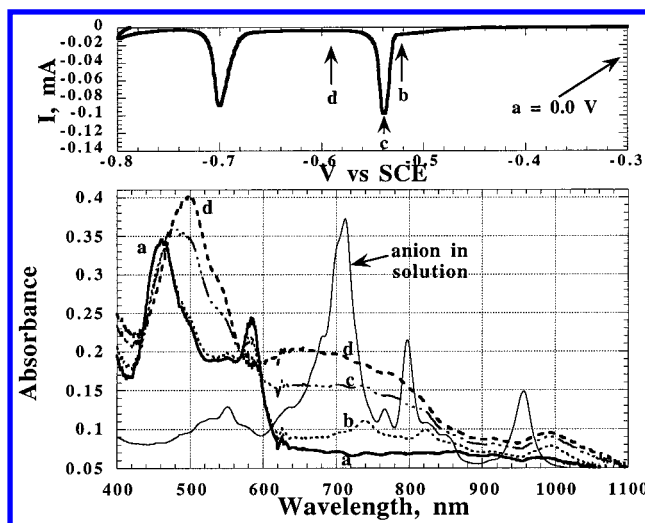


Figure 2. Absorption spectra of the PPEEB film as it is reduced through the first reduction wave. The labels on the spectra correspond to the potentials shown in the cyclic voltammogram. The spectrum of the anion in solution (DMF:H₂O, 4:1, contaminated with a small amount of the dianion absorbing at 551 nm) is shown for comparison.

of the electrochemically cycled film as that of a solvent-swollen film that may contain some electrolyte ions even in the neutral state.

At potentials in the prewave portion of the first reduction (spectrum "b", Figure 2), the absorbance of the short-wavelength peaks at 460 and 583 nm of the PPEEB film decreases while three long-wavelength absorbance peaks appear at 738, 821, and 993 nm. The three long-wavelength peaks resemble those of the anion in solution at 712, 798, and 956 nm. In this potential range, the spectrum of the reduced film resembles a mixture of the neutral species and the anion in solution. There is an apparent isosbestic point at 602 nm. Then, as the potential moves through the main reduction peak (spectra "c" and "d", Figure 2), a second optical transition is observed: a new short wavelength peak grows in at 497 nm, and the two higher energy anion-like peaks (738 and 821 nm) are replaced by a broad absorbance from 600 to 900 nm. This transition shows an isosbestic point at 570 nm. These spectra no longer resemble the anion in solution. Consistent with the cyclic voltammetric results, if the scan is reversed in the prewave at -0.52 V, the peaks at 738 and 821 nm reversibly decline. But if the scan is reversed after the main reduction peak at -0.54 V, the peak at 497 nm declines upon reoxidation (-0.42 V), but the peaks at 738 and 821 nm do not reappear. These results are consistent with a change in film structure upon reduction past the prewave (~ 0.15 equiv) to a structure in which the anion is stabilized, as shown in Scheme 1.

Reduction of the anion to the dianion (Figure 3) results in the disappearance of the peak at 497 nm and the appearance of a new peak at 546 nm, similar to the absorbance maximum of the dianion in solution at 551 nm. There is an isosbestic point at 390 nm (not shown). Another new peak appears at 425 nm. The longest wavelength band of the anion at 993 nm also decreases upon reduction to the dianion, and the broad absorbance between 600 and 900 nm becomes a long-wavelength shoulder on the dianion peak at 546 nm. Reoxidation of the dianion at -0.62 V leads to the decline of the peak at 546 nm and the growth of the peak at 497 nm. That is, the optical transition seems completely reversible except for the potential offset caused by the structural rearrangement.

The spectroelectrochemical results are consistent with, and provide insight into, the cyclic voltammetric data. The evolution

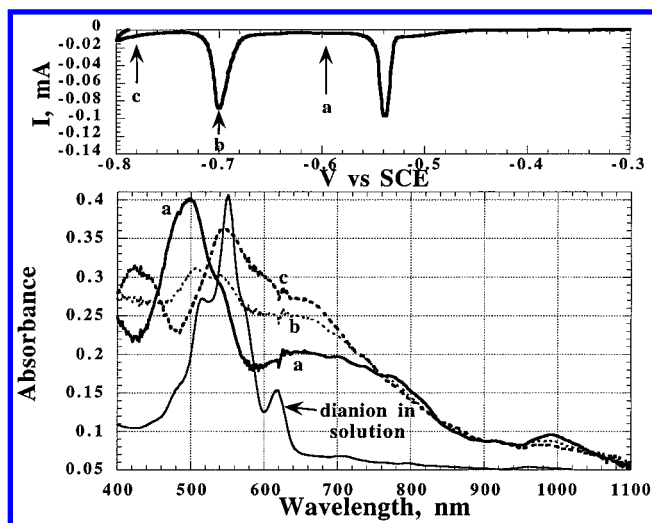


Figure 3. Absorption spectra of the PPEEB film as it is reduced through the second reduction wave. The labels on the spectra correspond to the potentials shown in the cyclic voltammogram. The spectrum of the dianion in solution (DMF:H₂O, 4:1) is shown for comparison.

of the absorption spectra with potential suggests the presence of three distinct reduced species. The first closely resembles the anion in solution and is present only in the prewave before the first reduction peak. Reduction past this point leads to the disappearance of this species and the appearance of a new anionic species consistent with a structural rearrangement of the film to a form that stabilizes the anion. Further reduction leads to the appearance of the final species with a spectrum similar to the dianion in solution but with the enhanced low-energy absorbance indicative of intermolecular interactions.

Conductivity vs Potential Measurements. A 100 nm film of PPEEB was spin-coated over an interdigitated array electrode (Au-IDE) consisting of two sets of 50 gold fingers. A cyclic voltammogram (Figure 4) was recorded at a scan rate of 0.6 mV/s with the two arrays connected together. At this slow scan rate, the CV looks similar to that on the SnO₂ electrode shown in Figure 1, except there are tails on the peaks caused by the lateral diffusion of charge and compensating ions between the two arrays of electrodes. At faster scan rates, this diffusional process causes shoulders to appear on the CV peaks.

A second CV experiment was performed at the same scan rate with a 10 mV offset between the two electrode arrays. In this experiment there are two components to the current: one from the reduction and reoxidation of the film, i_{CV} , as in the previous experiment, and an additional component, i_o , from the current flowing between the two sets of electrodes driven by the 10 mV offset voltage. This latter current, which is much greater than i_{CV} over most of the potential range, is proportional to the redox conductivity^{34–36} of the film and is obtained from

$$i_o = (i_1 - i_2)/2$$

where i_1 and i_2 are the currents from the two sets of array electrodes. Since i_{CV} is a component of the current in both electrodes, subtracting the two eliminates i_{CV} . The scan rate, 0.6 mV/s, was slow enough to ensure quasi-steady-state conditions, an important requirement for the validity of the measurement.^{35,36} Doubling the scan rate had no effect on the measured conductivity. The potential resolution of this technique is limited by the offset voltage, 10 mV in our experiments. The use of IDEs to measure the conductivity of polypyrrole at set potentials was first described by Wrighton and co-workers.³⁷ Murray and co-workers have employed similar techniques to

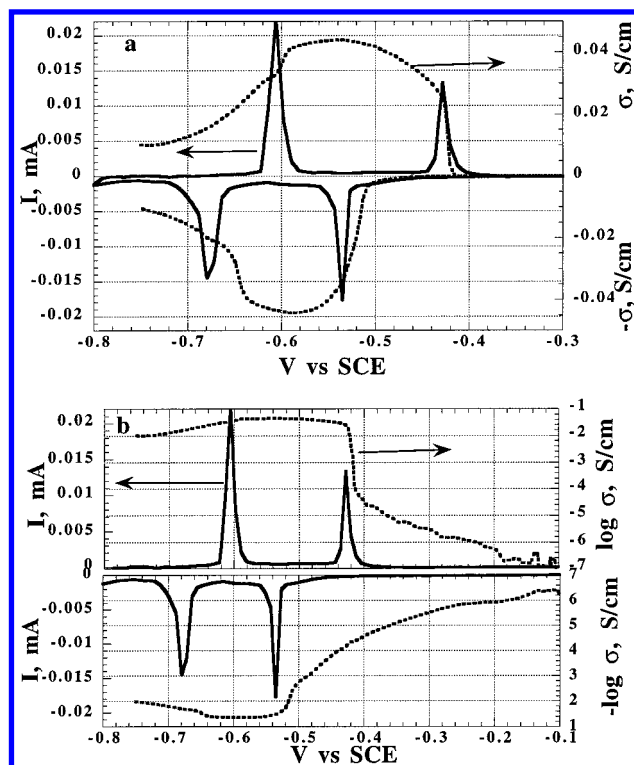


Figure 4. Redox conductivity, σ , of the PPEEB film as a function of its state of reduction. The cyclic voltammogram of the film at a scan rate of 0.6 mV/s on the Au interdigitated array electrode is also shown. (a) Conductivity on a linear scale that emphasizes the maximum in σ in the anionic state and the decrease in the dianionic state. (b) Conductivity on a logarithmic scale and an expanded voltage range that emphasizes the sharp decrease upon reoxidation to the neutral state (-0.42 V) and the gradual change in σ positive of the first noticeable reduction.

measure the redox conductivity and the diffusion coefficients of electrons in redox polymer films.^{34,38} The technique of scanning both array electrodes with a small, fixed potential difference between them has been employed for measuring the conductivity vs potential of redox polymers,³⁵ of polypyrrole,³⁹ and of cathode materials for lithium batteries^{40,41} but apparently has not been used previously for the study of molecular semiconductor films.

Because this experiment is carried out in the presence of excess electrolyte, the applied potential drops close to the electrodes and leaves essentially no electric field in most of the gap between the electrodes. Therefore, what is measured is not the electronic conductivity but the redox conductivity, in which charge carriers are driven by a concentration gradient rather than by an electric field.^{34,38} In potential-resolved conductivity measurements,^{35,36} the offset voltage is kept constant with potential and is small enough that the induced current is a linear (ohmic) function of the voltage. Therefore, the redox conductivity is calculated from^{35,39,41}

$$\sigma = i_o/EA$$

where E is the voltage offset between the electrodes divided by the distance between them and A is the total effective area between the two arrays of electrodes. Since we employed PPEEB films of approximately the same thickness as the electrode fingers, A is determined by the thickness of the electrodes (0.11 μm) and their total length (50 cm) leading to $A = 5.5 \times 10^{-4} \text{ cm}^2$. The measured spacing between the electrodes was 11.5 μm ; thus, $E = 8.7 \text{ V/cm}$ for an offset voltage of 10 mV.

The redox conductivity vs potential measurements of the PPEEB film are shown in Figure 4a,b, superimposed over the CV of the same film. These results are reproducible ($\pm 20\%$ in σ , almost exact in potential dependence) from film to film and over multiple scans of the same film. The conductivity increases rapidly as the potential is scanned through the prewave, reaching 60% of its maximum value by -0.52 V, a potential at which only $\sim 15\%$ of the film is reduced. It then increases more slowly as the film becomes completely reduced to the anion, reaching a maximum value of 4.4×10^{-2} S/cm at -0.59 V vs SCE. The conductivity then decreases as the film is reduced to the dianion. Reversing the scan direction causes the conductivity to increase again as the dianion is oxidized back to the anion. After reaching a maximum when the film is almost completely in the anionic form, the conductivity drops extremely rapidly (3 orders of magnitude in 30 mV, Figure 4b) as the anion is oxidized back to the neutral species.

The conductivity of the dry film measured before the electrochemical experiments was 10^{-12} S/cm. Upon electrochemical doping, the conductivity of the PPEEB film increases by about 10 orders of magnitude. The magnitudes of the conductivity in both undoped and doped states are in the range expected from measurements on other molecular semiconductors.

There are only a few previous studies of the change in conductivity of molecular semiconductors as a function of oxidation state. They involved preparing the compound in specific oxidized or reduced states and then measuring the conductivity of that state by the four-point probe technique.^{19–21,42–44} This procedure has the advantage of measuring an electronic conductivity rather than a redox conductivity on a dry, or purposely wetted, sample of known composition. It has the disadvantage that it is difficult (impossible with some compounds) and time-consuming to prepare and isolate samples in a number of different oxidation states. Perhaps for these reasons, few high-resolution measurements of conductivity vs potential have been reported for molecular semiconductors.^{19,42,44} The electrochemical technique used here³⁵ allows redox conductivity measurements at an effective resolution of 10 mV to be made over a large potential range on a single sample. However, the film composition and structure may change during the potential scan due to incorporation of solvent and electrolyte ions and phase changes in the film. Furthermore, the exact relationship between the electronic conductivity and the redox conductivity is still unclear. In some cases the conductivity increases several orders of magnitude when a dry sample is swollen by solvent,^{21,43} and in other cases the conductivity of the dry sample is much higher than the solvent-swollen one.³⁶ Nevertheless, we expect that the redox conductivity vs potential measured here will be related to that measured in dry samples without excess electrolyte ions, and experiments to test this proposition are in progress.

The maximum redox conductivity reached by the polycrystalline PPEEB films in our experiments was 4.4×10^{-2} S/cm. This compares to the following values for the electronic conductivity of other molecular semiconductors measured by the four-point probe technique: a film of naphthalene diimide anion complexed with a polycation showed a conductivity of 10^{-4} S/cm when dry and 10^{-1} S/cm at 90% humidity.²¹ A dendrimer containing naphthalene diimide anion had a conductivity of 0.12 S/cm when dry and 11 S/cm at high humidity.^{21,43} Polycrystalline samples of partially oxidized polymeric silicon phthalocyanine reached a conductivity of 10^{-1} S/cm at room temperature.⁴² Single crystals of free base phthalocyanine one-third oxidized with iodine showed a conductivity of 700 S/cm

along the stacking direction and about 1 S/cm perpendicular to this axis.¹⁹ Polycrystalline samples of stacked phthalocyanines have shown conductivities of 10^{-11} – 10^{-1} S/cm depending on doping level, metal derivative, and bridging ligand.²⁰

It is expected that the conductivity of an organic material will reach its maximal value at a state of partial oxidation (reduction),¹⁹ in contrast to the results shown in Figure 4 where the conductivity is maximized for the fully reduced (anionic) PPEEB. The few previous studies of conductivity vs potential in molecular semiconductors have shown the expected maximum in conductivity at states of partial oxidation (reduction). The conductivity of polymeric silicon phthalocyanine doped with TCNQ reached its maximum value between 25% and $\sim 60\%$ oxidation and decreased by about a factor of 10 when completely oxidized to the cation.¹⁹ The conductivity increased again as the cation was partially oxidized to the dication. The conductivity of a film containing half-reduced naphthalene diimide (half anion/half neutral) attached to a dendrimeric backbone was 30 times higher than a similar film that was completely reduced (all anion).⁴³

The conductivity of molecular semiconductors increases when they are partially oxidized or reduced because of the increase in the number of “free” charge carriers that can move through the films. However, the conductivity is expected to decrease again when the materials are oxidized or reduced by integral numbers of electrons because the Coulombic repulsion energy between two charge carriers on a single molecule is usually larger than the bandwidth of the material; this is the Mott insulator state.¹⁹ Therefore, it is surprising that PPEEB films exhibit their maximum conductivity when they are reduced by approximately one electron per molecule. The reasons for this are not yet understood but may be related to the difference in the methods of measuring conductivity in our study compared to previous studies of molecular semiconductors. Because of the availability of excess (and small) electrolyte ions in our electrochemical measurements, the Coulombic repulsion energy between two electrons on the same perylene diimide molecule may be reduced to less than the width of the conduction band. In this case, the conductivity should decrease only when the conduction band becomes filled by further reduction of the anion to the dianion, as observed in our experiments. Further studies will be required to understand this point.

The conductivity increases by 2 orders of magnitude as the electrochemical potential changes from -0.1 to -0.4 V, before any noticeable electrochemical reduction takes place (Figure 4b). In the usual model of semiconductors, this corresponds to moving the Fermi level closer to the conduction band edge and should increase the population of “free” electrons. At -0.4 V, less than 1% of the perylene diimide molecules are reduced, yet the conductivity (10^{-4} – 10^{-5} S/cm) is well within the semiconducting range and 7–8 orders of magnitude higher than the as-spin-coated, dry film. For photovoltaic applications it may not be necessary to go beyond this potential range, that is, beyond the $\sim 1\%$ doping level. Further experiments to measure the dependence of the photophysical and photovoltaic properties of perylene diimide films on the electrochemical potential are in progress.

Summary

Thin films of liquid crystal perylene diimide have been characterized by electrochemical methods. They show strong attractive intermolecular interactions when electrochemically reduced and apparently undergo structural rearrangements that stabilize the reduced forms. The redox conductivity of the films

has been measured between -0.1 and -0.8 V vs SCE. The conductivity increases by about 2 orders of magnitude before any noticeable electrochemical transition occurs and then increases another 3 orders of magnitude upon reduction to the monoanion. Further reduction to the dianion decreases the conductivity by a factor of 4. The conductivity increases to well within the semiconducting range before even 1% of the film is reduced, suggesting that less than 1% doping may be required for photovoltaic applications.

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