An Investigation of the Effect of Pyridine Derivatives on the Oxidative Polymerization Process of 2,5-Dimercapto-1,3,4-thiadiazole and Its Disulfide Dimer

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The effects of pyridine and several derivatives (3-chloropyridine and lutidine) on the redox reactions of 2,5-dimercapto-1,3,4-thiadiazole (DMcT) and the disulfide dimer of DMcT have been examined using cyclic voltammetry and UV−vis spectroscopy. In the presence of these bases, the oxidative coupling reactions of DMcT and its disulfide dimer to give a disulfide-containing polymer are facilitated, presumably due to proton-transfer processes with the bases. The potentials at which the oxidative polymerization and reductive depolymerization occur in the presence and absence of such proton transfer reagents are discussed. Also, it is observed that the oxidation of DMcT is facilitated in the presence of DMSO or NMP. The relevance of these results to the possible use of DMcT/polyaniline composite materials as a cathode material in secondary lithium batteries is discussed, especially with regard to the potentials at which the various redox processes can occur.

Introduction

Historically, 2,5-dimercapto-1,3,4-thiadiazole (DMcT) and related compounds have been widely studied for their behavior as bioactive compounds,[1] metal chelating agents,[2−5] and antioxidants and antiwear agents.[6] More recently, these compounds have received some attention as components of a candidate cathode material for lithium secondary batteries.[7−17] This application is based on the reversible redox reactions of the thiol/disulfide redox couples of such compounds. A previous example of the use of thiol/disulfide redox couples as an energy storage system employed a molten salt of the sulfur compound at high temperature.[8,9] In that case, high temperature was required because the thiol/disulfide redox reaction is normally slow at room temperature. Recently, Oyama and co-workers have overcome this problem by using polyaniline (PAn) to catalyze the redox reaction of DMcT.[10−14,18] Composite cathode materials made from PAn/DMcT mixtures have been shown to exhibit some of the highest energy densities yet reported for Li secondary batteries.[19] For these materials, the redox reaction involves oxidation of DMcT to produce a disulfide-containing polymer during charging and reductive depolymerization during discharge. From a kinetic standpoint, the important process during discharge is the reductive cleavage of the S−S bond. In this regard, a key question relates to the mode of action of PAn in accelerating this process. Several possibilities exist, a likely one being proton transfer (from PAn to the S−S bond) during the reduction process.[14−16] However, the complex nature of the PAn/DMcT composites makes detailed study of these reactions very difficult. To simplify the elucidation of proton-transfer effects in DMcT redox chemistry, we have undertaken to study it in the presence of simple acid/base systems, such as pyridine and its derivatives. This report describes efforts toward this end.

In comparison with many other thiol compounds, a distinguishing feature of DMcT and its derivatives is the possibility of tautomeric structures having either the thioamide (−NH−
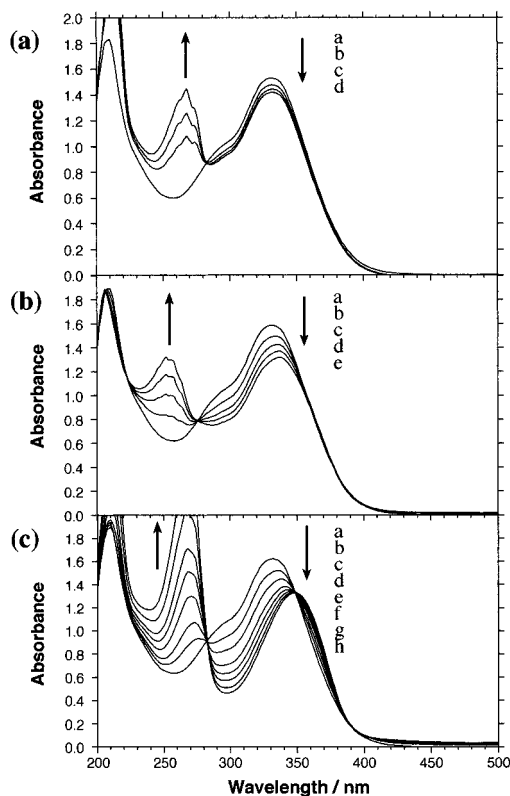
C(=S)−) or the thiol (−N=C(SH)−) form.[20,21] For DMcT, it is also known that the first pK_a is unusually low for a thiol compound, being observed at −1.36.[15,21−25] The effects of tautomerization on the redox chemistry of such compounds do not appear to have been investigated and, therefore, present a complication in understanding the redox chemistry of this class of compounds. Previous electrochemical results have shown that DMcT exhibits redox waves that are typical for oxidation of a thiol group to give a disulfide and for reduction of a disulfide to give the original thiol form.[15,16] In aprotic media, the potential at which oxidation is observed for DMcT (0.95 V) and its derivatives is significantly lower than that for other thiols that are not capable of tautomerization; e.g., thiophenol and butanethiol show oxidation peak potentials at 1.32 and 1.34 V, respectively.[26] When strong bases are present, DMcT exists in the thiolate form, thereby removing the influence of such tautomerization. Thus, another motivation for the present investigation was to investigate DMcT redox chemistry under conditions in which the tendency for tautomerization can be varied (or eliminated).

Previous work has presented some preliminary information about how acid/base chemistry affects the redox processes of DMcT and its derivatives.[15−17] For example, it has been shown that the electrochemistry of DMcT in γ-butyrolactam is consistent with the behavior of DMcT⁻, the singly deprotonated form of DMcT, which suggests loss of H⁺ from DMcT (a strong acid) in that medium prior to oxidation.[15] The influences of triethylamine (TEA) and pyridine as proton acceptor and methanesulfonic acid as proton donor have also been briefly described.[16,17] In the case of TEA, the first equivalent produces DMcT⁻ and the second equivalent produces DMcT²⁻, the doubly deprotonated form of DMcT, and the voltammetry and UV−vis spectroscopy are entirely consistent with this. For pyridine, the situation is more complicated because it is capable of effecting the first deprotonation to produce DMcT⁻, but not the second. This creates a situation in which the single oxidation peak (0.95 V vs Ag/AgCl) of DMcT is split into two clear waves (+0.25 and +0.7 V), and the corresponding reduction peak current is drastically enhanced.[15] Further, as will become more

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SCHEME 1


Figure 1. UV−vis spectra of DMcT (1 mM) with (a) 3-chloropyridine, (b) pyridine, and (c) lutidine in AN. In each spectrum, the concentration ratio [3-chloropyridine, pyridine, or lutidine]/[DMcT] corresponds to (a) a = 0.0, b = 0.5, c = 1.0, d = 1.5, e = 2.0 and (b, c) a = 0.0, b = 0.5, c = 0.75, d = 1.0, e = 1.5, f = 2.0.

clear in this contribution, the influence of pyridine and its derivatives on the redox chemistry of DMcT and its derivatives is dependent on the pK_a's of the pyridine derivatives. It is a purpose of this paper to experimentally explore that dependence using UV−vis spectroscopy and cyclic voltammetry.

Several other investigators have employed the strategy of examining redox driven polymerization processes of various types of monomers by extending their studies to the same (or similar) reactions of the dimers. For example, production of polypyrrole was examined in this way,[27] as was the production of polythiophene via oxidative polymerization of bithiophene.[28] In the present case, the use of the DMcT disulfide dimer (see Scheme 1) as a starting material for oxidative polymerization to produce the polymeric disulfide has provided additional insight into the reaction pathways for this system, especially with regard to the potentials required to effect the various redox processes.

Experimental Section

Materials. Acetonitrile (AN), dimethyl sulfoxide (DMSO), *N*-methylpyrrolidone (NMP), and methanol were purchased from Aldrich Chemical and purified by distillation in the usual manner. DMcT, pyridine, 3-chloropyridine, lutidine, and iodine were also purchased from Aldrich Chemical. The DMcT dimer was prepared by chemical oxidation with I$_2$, as previously reported.[15] The crude product was purified twice by recrystallization from methanol.

Electrochemical Measurements. The cyclic voltammograms of DMcT and its dimer were obtained using a potentiostat (BAS model CV27) and an *X*−*Y* recorder (Hewlett-Packard model 7142A) and are reported vs Ag/AgCl/NaCl(sat.). Measurements were carried out in a three-electrode cell using a glassy carbon disk electrode (BAS, diameter 3.0 mm) as the working electrode, a platinum wire (diameter 0.5 mm, length 60 cm coil) as the counter electrode, and Ag/AgCl/NaCl(sat.) as a reference electrode. All measurements were done at 25.0 ± 0.1 °C, at a scan rate of 50 mV s^{-1}, and in acetonitrile (AN)

containing 0.2 M LiClO$_4$, unless otherwise noted. A few experiments were done in DMSO or NMP containing 0.2 M LiClO$_4$. All solutions were extensively deaerated using nitrogen gas prior to experiments.

UV−vis Spectroscopy. The UV−vis spectra were obtained using a diode array type UV−vis spectrometer (Hewlett-Packard HP8452). Measurements were done using a quartz cell (optical length 1 mm, width 10 mm). Considerable care was taken to ensure the exclusion of both oxygen and water from the samples during the measurements.

Results and Discussion

UV−vis Spectroscopy. Knowledge of the conditions under which the various acid/base forms of DMcT and its disulfide dimer will exist is essential to unraveling the influence of the pyridine derivatives on their electrochemical responses. Thus, we first discuss the UV−vis spectroscopy of these systems as a means of evaluating their acid/base chemistry. In considering these data, it is worth keeping in mind the relative pK_a's of these compounds. In aqueous solution, 3-chloropyridine, pyridine, and lutidine have pK_a values 2.81, 5.23, and 6.90,[29,30] respectively. The first deprotonation of DMcT occurs at −1.76 and the second at 7.5.[24] Of course, these aqueous pK_a values do not pertain directly to the behavior that will be observed in AN solutions. However, they do serve to illustrate the relative acidity of these compounds.

Figure 1 shows UV−vis data on the effect of addition of 3-chloropyridine, pyridine, and lutidine to an AN solution of DMcT. Considering the case of lutidine (the strongest base, Figure 1c) first, one can see the increase of a peak at 352 nm and the simultaneous decrease of a peak at 320 nm as lutidine

Figure 2. UV–vis spectra of DMcT dimer (1 mM) with (a) 3-chloropyridine, (b) pyridine, and (c) lutidine in AN. In each spectrum, the concentration ratio [3-chloropyridine, pyridine, or lutidine]/[dimer] corresponds to (a) a = 0.0, b = 1.0, c = 2.0, d = 4.0, (b) a = 0.0, b = 1.0, c = 2.0, d = 3.0, e = 4.0, and (c) a = 0.0, b = 0.25, c = 0.5, d = 1.0, e = 1.5, f = 2.0, g = 3.0, h = 4.0.

is added. These peaks have been previously assigned to DMcT$^-$ and DMcT, respectively.[15] Essentially all of the spectral changes are completed after the addition of one molar equivalent, with only very minor spectral changes associated with the addition of a second molar equivalent. One can also clearly observe an isosbestic point at 331 nm. These spectral changes point to the deprotonation of DMcT by lutidine. However, as pointed out previously,[15] the very similar spectra of DMcT$^-$ and DMcT^{2-} make it extremely difficult to determine whether lutidine is capable of producing DMcT^{2-}. It is worth noting that the spectra in Figure 1c are virtually identical with those observed for addition of up to two molar equivalents of triethylamine (TEA) to DMcT.[15] In that case, it was demonstrated from the electrochemical response that TEA can effect both deprotonations.

Essentially identical data are observed for the case of pyridine in Figure 1b. Again, the first deprotonation is clearly effected by the first molar equivalent of pyridine, while the second is uncertain. For both the pyridine and lutidine cases, the increase of the peak at 352 nm is directly proportional to the increase in the concentration of base, indicating a one-to-one proton-transfer reaction of the base with DMcT to produce DMcT$^-$. For 3-chloropyridine, on the other hand, the spectra make clear that the pK_a of this compound is not sufficiently large to fully deprotonate DMcT, even after the addition of two molar equivalents. However, the spectra do indicate that some deprotonation occurs (Figure 1a).

The behavior of the DMcT dimer in the presence of these pyridine derivatives is in contrast to that of DMcT itself. Figure 2 shows the spectra for sequential addition of up to four molar equivalents of each base. In the case of 3-chloropyridine (Figure
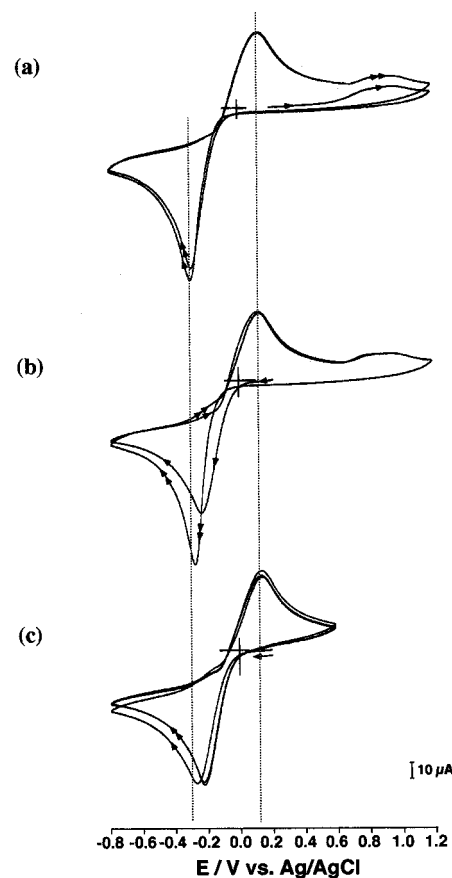
Figure 3. Cyclic voltammograms of DMcT dimer (5 mM) in AN containing 0.2 M LiClO$_4$. The difference between (a), (b), and (c) is the initial direction of the potential scan, which is indicated by the arrows, and the potential limits. For (a) and (b) the limits were −0.8 and 1.2 V, while for (c) the limits were −0.8 and +0.6 V. Scan rate was 50 mV/s.

2a), the spectral changes are minimal, suggesting that this base is too weak to effectively deprotonate DMcT. For pyridine (Figure 2b), slightly more evolution of the spectra occurs, suggesting some deprotonation, but not on a one-to-one molar basis. For lutidine, the spectral changes are much more apparent, but again do not appear to occur on a one-to-one molar basis.

Electrochemistry. Preliminary data illustrating the behavior of DMcT in the presence of pyridine were reported previously.[15] Briefly, in pure AN supporting electrolyte, one observes an oxidation peak at 0.95 V and a weak reduction peak at −0.3 V. Addition of one molar equivalent of pyridine produces DMcT$^-$, which exhibits a quasi-reversible electrochemical response with an oxidation peak at 0.15 V and a reduction peak at −0.2 V. The oxidation of DMcT at 0.95 V and that of DMcT$^-$ at 0.3 V produce the DMcT dimer, as shown in Scheme 1a,b. If an additional molar equivalent of pyridine (for a total of two) is added, a second oxidation peak at 0.65 V is observed, which produces the disulfide polymer of DMcT (Scheme 1c).
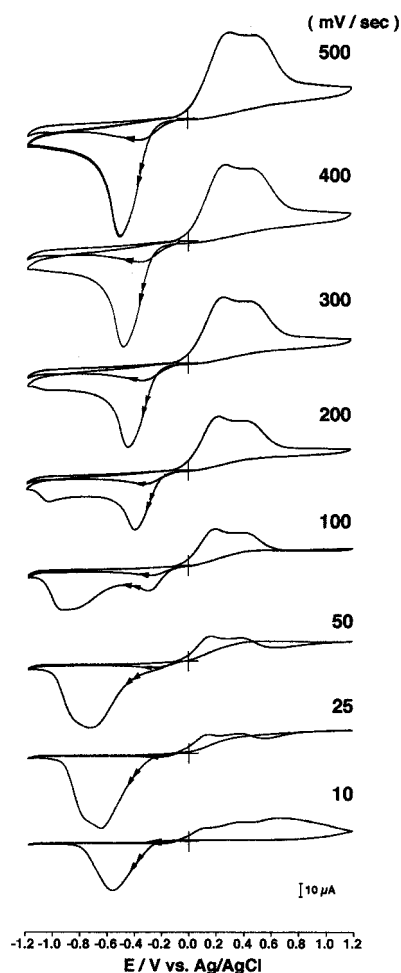
The redox behavior of the DMcT dimer in pure AN supporting electrolyte is shown in Figure 3. This compound exhibits a quasi-reversible electrochemical response with a reduction peak at ca. −0.2 V and a corresponding oxidation peak at 0.15 V. These result from reductive cleavage of the disulfide bond to give DMcT$^-$ and its subsequent oxidation back to the disulfide dimer, respectively. A small oxidation wave is also observed at ca. 0.8 V. This appears to result either from an impurity of DMcT in the sample (elemental analysis[15] does

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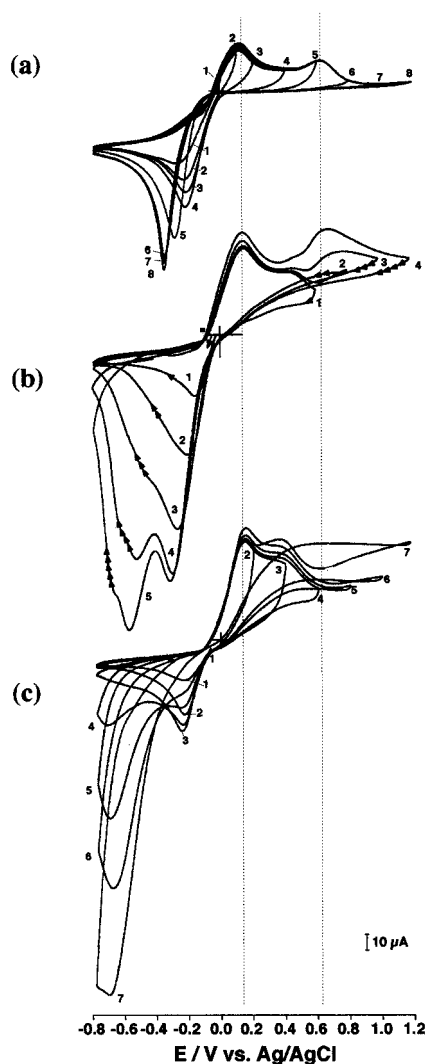
Figure 4. Repetitive cyclic voltammograms of DMcT dimer (5 mM) in AN containing 0.2 M LiClO$_4$ with (a) 3-chloropyridine (10 mM), (b) pyridine (10 mM), and (c) lutidine (10 mM). Scan rate was 50 mV/s. In all cases, the initial scan direction was negative, starting at ca. 0.0 V. The numbers refer to consecutive scans in which the positive limit was increased each time.

Figure 5. Scan rate dependence of the cyclic voltammetry of the dimer−lutidine system in AN containing 0.2 M LiClO$_4$.

not provide definitive differentiation of these two compounds) or from a small amount of dimer polymerization at that potential. As can be seen, scanning over this wave produces slight changes in peak shape for the reduction at −0.2 V, which may be due to deposition of polymeric material on the electrode surface. This "phaselike behavior" has been previously discussed in the context of polymeric deposits on electrode surfaces.[15,31−33]

The redox behavior of the dimer (5 mM) in the presence of the bases (10 mM) is shown in Figure 4. As can be seen, the behavior is quite complex and depends on the range of potentials over which the scan is made. In every case, if the positive potential limit is restricted to values less than about 0.3 V, one observes the same quasi-reversible electrochemical response that was observed in the absence of the bases, i.e., reductive cleavage to give DMcT$^-$ and reoxidation to give the disulfide dimer. However, if the potential limit is made more positive, additional oxidation processes are observed. In the case of 3-chloropyridine (Figure 4a), one observes a new anodic wave at 0.65 V. Scanning over this wave leads to shape changes for the reduction at −0.2 V, just as was the case for the dimer in the absence of base, suggesting deposition of some material on the electrode surface. For pyridine, two new oxidations are observed at 0.4

and 0.65 V. Scanning over the second of these leads to the appearance of a very large reduction wave at −0.6 V which grows larger as this wave is repeatedly traversed. This second oxidation wave is attributed to dimer oxidation to give the disulfide polymer (Scheme 1c), and the reduction at −0.6 V is attributed to its subsequent reduction to produce DMcT$^-$. Production of DMcT is not possible under these conditions because of its strong acidity, and production of DMcT^{2-} is also not possible, because it would be protonated by the pyridinium species that are present near the electrode surface.[15] Figure 4c shows the behavior in the presence of lutidine. In this case, the additional oxidation processes (a peak at 0.4 V and a rising anodic plateau beginning at 0.65 V) cause drastic changes in the shape of the voltammetric response. Repeated cycling over the range −0.8 to 1.2 V leads to disappearance of the dimer reduction at −0.2 V and the appearance of a very large reduction at ca. −0.7 V, again consistent with a buildup of the disulfide polymer on the electrode surface. It is interesting to note that the tendency to produce this polymeric material is increased as the pK_a of the base is increased, clearly showing that proton transfer is an important process in its production.

Figure 5 shows the scan rate dependence of the redox processes for the dimer/lutidine system (5 and 10 mM, respectively). These data show a broad oxidation in the range 0.0−1.2 V, with peaks at about 0.2 and 0.4 V. This oxidation undoubtedly produces the disulfide polymer. The data also show two distinct reductions, centered at −0.6 and −1.0 V (at a scan rate of 200 mV/s). At higher scan rates, only the first (less negative) reduction is observed. This peak shifts in the

positive direction with decreasing scan rate, suggesting kinetic limitations at higher scan rates. As scan rate is decreased and the time allowed for production of the disulfide polymer increases, one observes a decrease in the intensity of the wave at -0.6 V and a corresponding increase in that of the peak at -1.0 V. This peak also shifts in the positive direction with decreasing scan rate, again suggesting kinetic limitations at higher scan rates. While we cannot offer a definitive explanation of the origins of these two reduction peaks, we speculate that they correspond to the reductive cleavage of the disulfide polymer that is either facilitated by proton transfer from pyridinium (peak at -0.6 V) or not (peak at -1.0 V). Thus, the reduction at -0.6 V would correspond to the production of DMcT$^-$, while that at -1.0 V would correspond to production of DMcT^{2-}. This large change in driving force for reduction due to the availability of proton donors is consistent with previous observations of the influence of proton transfer in this[15] and other[34–38] thiol/disulfide redox systems. A likely cause of this change in reduction pathway would be reduced access of pyridinium cations (the proton donor) into the interior of the polymeric material as scan rate decreases and film thickness increases.

Solvent Dependence. Given the strong dependence of DMcT redox chemistry on proton acceptors, the behavior in DMSO and NMP was examined. Wallace and co-workers have previously reported that DMSO facilitates the oxidation of thiols, especially aromatic thiols.[36–38] This tendency is reflected in its high (Gutmann) donor number,[39] implying good basicity and proton acceptor character. The donor numbers of AN, DMSO, and NMP are 14.1, 29.8, and 27.3, respectively.[39] Based on their high donor numbers and the previous work by Wallace, it was expected that both DMSO and NMP would serve the same proton acceptor function as the pyridine bases during DMcT oxidation.

Figure 6 shows the UV–vis spectra of DMcT (Figure 6a) and its disulfide dimer (Figure 6b) in AN with increasing amounts of DMSO. The similarity of the spectra in Figures 6a and 1b makes it clear that that DMSO is capable of deprotonating DMcT, producing DMcT$^-$. On the other hand, the lack of significant spectral changes shows that there is no acid/base chemistry between DMSO and the disulfide dimer, as expected.

Figure 7 shows the electrochemical response of DMcT in AN (Figure 7c), NMP (Figure 7b), and DMSO (Figure 7a). It can be seen from these responses that, in both NMP and DMSO, DMcT exhibits redox behavior that is quite similar to that observed in AN solutions of pyridine and lutidine. In other words, this behavior is characteristic of the redox chemistry of DMcT$^-$.

Conclusions

This study has demonstrated the dramatic influence that proton acceptors and donors can have on the redox behavior of compounds such as DMcT and its disulfide dimer. Specifically, it has been shown that proton acceptors can greatly facilitate the oxidation of DMcT and its dimer to produce the disulfide polymer and that this behavior depends critically on the pK_a of the base. Further, the facilitation by proton donors of the reductive cleavage of the polymer to produce DMcT$^-$ or DMcT^{2-} has also been demonstrated. A more thorough study of the influence of proton donors on the reductive cleavage of disulfides of this type, including simulations of the electrochemical responses and a detailed kinetic treatment, has been submitted elsewhere.

These results are especially relevant to the use of the DMcT/disulfide polymer redox couple as a cathode material in Li
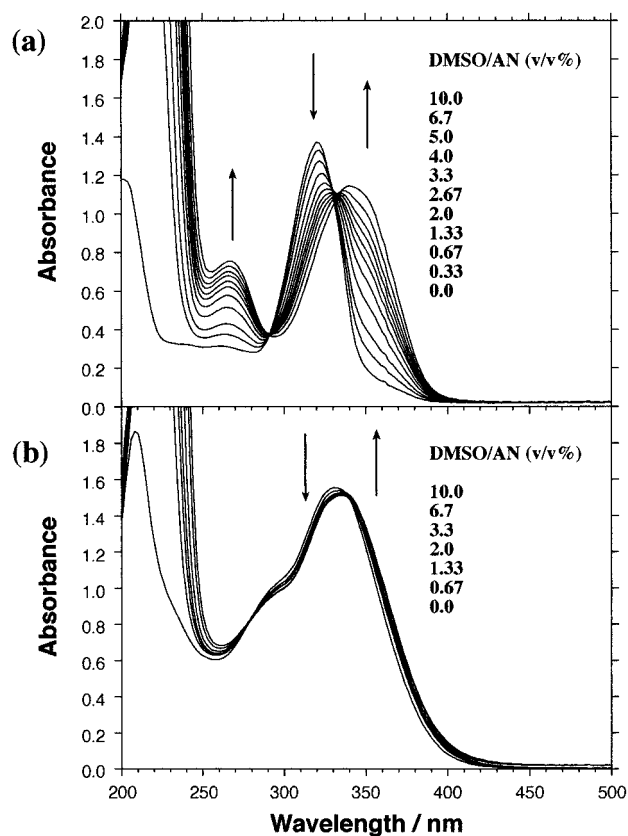
Figure 6. UV–vis spectra of (a) DMcT (1 mM) in AN containing various volume percents of DMSO and (b) DMcT dimer (1 mM) in AN containing various volume percents of DMSO.
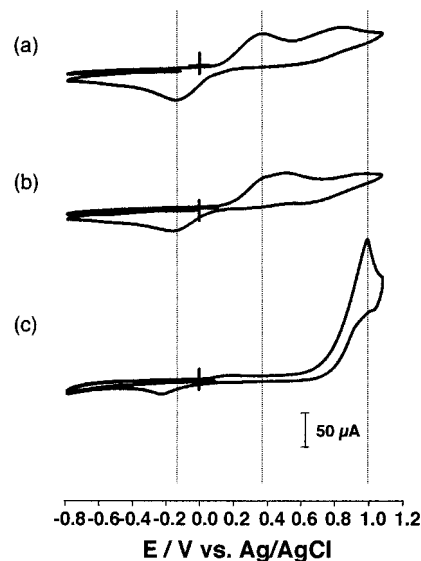
Figure 7. Cyclic voltammograms of DMcT in (a) DMSO, (b) NMP, and (c) AN solutions containing 0.2 M LiClO$_4$. Scan rate was 50 mV/s.

secondary batteries. In that application, it is generally assumed that the cathodic part of the discharge process corresponds to reduction of the disulfide polymer to the dithiolate, DMcT^{2-}.[19] The potential at which this occurs has a significant impact on the attractiveness of the cathode material, with more positive potentials being more desirable. In addition, the identity of the reduction product (e.g., DMcT$^-$ versus DMcT^{2-}) figures significantly in the theoretical calculations of energy density for these cathodes. Recent work has demonstrated that conducting polymers, such as polyaniline (PAn) and polypyrrole can

influence the charge and discharge processes for this system.[13,19] For example, when DMcT is intimately mixed with PAn to produce a composite material, this reduction of the disulfide polymer appears to occur at remarkably positive potentials, in the range +0.3 to +0.5 V.[13,19] In contrast, the data in Figure 5 clearly show that this reduction occurs at potentials as negative as −1.0 V when the reduction is not facilitated by proton transfer from a proton donor. However, the data presented here and previously[15] also show that reduction can occur at more positive potentials if proton donors are available. Given that the potential required to produce DMcT^{2-} from the disulfide polymer is in the range −0.6 to −0.7 V (or more negative) and that the potential at which PAn is reduced to its insulating form in these media is in the range +0.3 to +0.5 V,[13,19] it seems very likely that the reduced form of PAn is incapable of reducing the disulfide polymer to DMcT^{2-}. Thus, we suspect that the true product of reduction in the DMcT/PAn composite cathode material is DMcT^{-}, which would have a significant impact on the calculation of energy density for this secondary cathode material.[19] Whatever the product(s) of reduction, this analysis argues that proton transfer is a key process in the redox chemistry between DMcT and PAn in the composite cathode material. Additional investigations to further elucidate the complex chemistry of this system are in progress.

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