Supporting Information

Synthesis, Computational and Electrochemical Characterization of a Family of Functionalized Dimercaptothiophenes for Potential Use as High-Energy Cathode Materials for Lithium/Lithium-Ion Batteries

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Characterization and Synthetic Details for the TBT Family Studied

All reactions were carried out under an atmosphere of dry nitrogen unless otherwise stated. Anhydrous diethyl ether, purchased from Fischer Chemicals, was stored over 3 Å molecular sieves and purged thoroughly with nitrogen. Anhydrous tetrahydrofuran (THF), purchased from EMD Chemicals, and anhydrous hexanes, purchased from Aldrich Chemical Co., were stored under dry, inert atmosphere and used as received. Acetyl chloride was purchased from Acros and used as received, and *n*-butyllithium (nBuLi), 2,5-dimethylthiophene, *n*-bromosuccinimide (NBS), and *N*,*N*,*N*',*N*'-tetramethylethylenediamine (TMEDA) were purchased from Aldrich Chemical Co. and used as received. 3-Methoxythiophene, 3-methylthiophene, 2,3,5-tribromothiophene were purchased from Lancaster. 3,4-Dibromothiophene,[1,2] 2,5-dibromo-3-methoxythiophene,[3] and 3,4-dimethylthiophene[1,4,5] were prepared via literature methods. 2,5-Dibromo-3,4-dimethylthiophene and 2,5-dimethyl-3,4-dibromothiophene were prepared via slight modifications of the literature as described below.[3,4,6,7] All compounds gave identical spectra to those reported in the literature.

^{1}H and ^{13}C NMR spectra were obtained in the designated solvents on either a Varian Mercury-300 MHz or Inova-400 MHz spectrometer. Mass spectra were recorded at The University of Illinois Mass Spectrometry Facility on the 70-VSE-A spectrometer purchased in part with a grant from the Division of Research Resources, National Institutes of Health (RR 04648). Infrared spectroscopy was performed on a Mattson Polaris spectrometer. Melting points were recorded on a MelTemp melting point device and are uncorrected. All dimercaptothiophenes synthesized were named using the Struct=Name algorithm function in ChemDraw 10.0.

Synthetic Methods

General Method 1: An oven-dried three-neck round-bottom flask equipped with stir bar and septa was placed under vacuum and nitrogen-backfilled three times. Anhydrous diethyl ether was then added via cannula and cooled to -78°C. Two equivalents of 2.5 M nBuLi in hexanes were added via syringe followed by drop-wise addition of the appropriate dibromothiophene derivative in ether. After 15-30 minutes, two equivalents of sulfur were added quickly and stirred for 20 minutes at -78°C and at 0°C after which three equivalents of acetyl chloride were added via syringe. The reaction was allowed to warm to room temperature overnight under nitrogen and then worked up by addition of a saturated solution of ammonium chloride followed by extraction with diethyl ether. The organic phase was washed several times with ammonium chloride solution and then dried over magnesium sulfate. The solvent was then removed *in vacuo* to give the crude product.

General Method 2: General Method 2 was a slight modification of General Method 1. Instead of the direct use of two equivalents of nBuLi and sulfur, an alternating addition of one

equivalent at a time of nBuLi followed by one equivalent of sulfur was used. This was then repeated and followed by quenching with acetyl chloride. After warming to room temperature overnight the reactions were worked up in the same manner.

General Method 3: An oven dried three-neck flask equipped with stir bar and septa was placed under vacuum and nitrogen-backfilled three times. Anhydrous diethyl ether was added via cannula followed by the thiophene derivative and the reaction cooled to -78°C. 2.1 equivalents of 2.5 M nBuLi in hexanes were then added via syringe and the reaction was brought to room temperature after which it was stirred for four hours. The reaction was then cooled to -78°C and two equivalents of sulfur added in one portion and warmed to room temperature for 30-60 minutes after which it was cooled again to -78°C. Acetyl chloride was then added via syringe and the reaction allowed to warm to room temperature overnight. These reactions were worked up identically to those in General Method 1.

Recrystallization Procedure for Thioacetates: After chromatography on silica, the thioacetate was dissolved in a minimal amount of hexanes in a 20 mL vial. The vial was removed from heat, sealed, and allowed to cool to room temperature slowly. On some occasions, long transparent needles formed at room temperature or upon standing in a refrigerator for an hour. Most cases, however, required slow cooling in a dry ice/acetone bath. The vial was placed in the bath, swirled and removed after a few seconds. This was repeated until crystal formation ceased and the solution was mostly colorless. The solution could be warmed to room temperature without loss of crystals and filtered. The impurities, which sometimes separated as a highly viscous orange oil, could be decanted away during the cooling process. TLC analysis of the oil indicated no useful product was being lost. Note that at this point, the majority of the unpleasant odor was removed in the filtrate. The final products usually had only a faint odor and could be

dealt with outside the fume hood. This procedure could be repeated, but one recrystallization was generally sufficient.

***S,S'*-Thiophene-2,5-diyl diethanethioate (1) and *S*-Thiophen-2-yl ethanethioate (10).**

In THF:[8] This was performed according to General Method 1 with the solvent being changed from diethyl ether to THF. 2.5 mL of thiophene (31.2 mmol), 31.0 mL of 2.5 M nBuLi in hexanes (78.1 mmol), 60 mL of THF, 2.50 g of sulfur (78.0 mmol), and 13.4 mL of acetyl chloride (187.4 mmol) were used. After multiple vacuum distillations (150°C at 12 mbar), 2.92 g (59%) of **10** were isolated as a slightly yellow oil. Recrystallization following the procedure outlined above afforded the material as a white solid, which could be filtered in a pre-chilled fritted funnel, and melt soon afterwards. IR (KBr) 2859.9, 2360.5, 1716.3, 1535.1, 1459.9, 1384.6, 1251.6, 1110.8, 1068.4, 948.9, 729.0, 609.4 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (dd, J = 1.3, 3.9 Hz, 1H), 7.15 (dd, J = 1.3, 2.3 Hz, 1H), 7.09 (dd, J= 5.26, 1.6 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 135.7, 131.9, 127.8, 125.0, 29.4. HRMS calcd. for $C_6H_6OS_2$ 157.98601. Found 157.986035 (Error = 0.2 ppm).

Via General Method 3: 5.0 mL of thiophene (59.4 mmol), 150 mL of diethyl ether, and 52.3 mL of 2.5 M nBuLi (130.7 mmol) were stirred for an hour at room temperature before a white solution with large amounts of precipitation began to form. After the reaction had stirred three additional hours at room temperature it was cooled to -78°C and 4.19 g of sulfur (130.7 mmol) were added. Upon warming to room temperature the solution began to turn yellow. After 90 minutes the reaction was cooled again to -78°C and 25.4 mL of acetyl chloride (356.5 mmol) were added. After warming to room temperature overnight a bright red solution and a red precipitate formed which could be taken up in water and the aqueous phase was thoroughly extracted with ether. Chromatography on silica gel with dichloromethane gave 9.27 g of **1** (67%)

as an orange oil that solidified slowly. Further purification via the method described above gave an analytically pure sample. MP: 72-73°C. IR (KBr) 3093.3, 2364.3, 1712.5, 1407.8, 1361.5, 1118.5, 962.3, 823.5, 614.2 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (s, 2H), 2.41 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 135.6, 131.3, 29.9. HRMS calcd. for $C_8H_8O_2S_3$ 231.96864. Found 231.968428 (Error = 0.9 ppm).

***S,S'*-Thiophene-3,4-diyl diethanethioate (2).**

S,S'-Thiophene-3,4-diyl diethanethioate **2** was prepared via General Method 2. 3.60 g of 3,4-dibromothiophene (14.8 mmol) and 40 mL of ether were used. Addition of the first equivalent of nBuLi (5.9 mL, 14.8 mmol) gave a pale yellow solution. After 30 minutes at -78°C the first equivalent of sulfur (0.47 g, 14.8 mmol) was added and the solution, upon warming to room temperature for an hour, became a creamy yellow. After cooling to -78°C the procedure was repeated to give a pale yellow solution. This was cooled to -78°C and 2.2 mL of acetyl chloride (31.0 mmol) were added. Upon warming overnight the reaction consisted of a yellow solution with a white precipitate. Standard workup followed by chromatography on silica with a mixture of dichloromethane:hexanes (1:1 volume ratio) increasing to 1:0 (R_f = 0.5) gave a white yellow solid which could be easily recrystallized from hexanes and dichloromethane to give 1.13 g of **2** as a light brown powder (33%). MP: 115-117°C. IR (KBr) 3106.8, 2364.3, 1697.1, 1432.9, 1349.9, 1128.2, 966.2, 811.9, 617.1 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (s, 2H), 2.37 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 132.6, 127.2, 30.1. HRMS calcd. for $C_8H_8O_2S_3$ 231.96864. Found 231.969019 (Error = 0.4 ppm).

***S,S'*-3-Methylthiophene-2,5-diyl diethanethioate (3).**

Via General Method 1: Attempts to generate **3** via lithium-halogen exchange in THF from 2,5-dibromo-3-methylthiophene were unsuccessful. Addition of the bromothiophene to nBuLi and nBuLi to the bromothiophene both failed.

Via General Method 3: Following the standard procedure 4.9 mL of 3-methylthiophene (51.0 mmol), 39.2 mL of 2.6 M BuLi in hexanes (101.9 mmol), and 100 mL of ether were combined. After four hours at room temperature the reaction was cooled to 0°C and 3.76 g of sulfur (117.2 mmol) were added. **NOTE: If the addition is performed too quickly and at too high a temperature, a violent reaction ensues**. The reaction vessel was resealed and the remaining orange solution was stirred for 30 minutes. After cooling to -78°C, 16.3 mL of acetyl chloride (229.3 mmol) were added and the reaction quickly turned white. After warming overnight to room temperature the reaction was subjected to standard workup and silica chromatography performed with hexanes switching to dichloromethane gave **3** as an orange oil. Distillation at 10 mbar gave a mixture of isomers of mono-substituted product from 110-200°C (0.83 g) and **3** at 250°C. This was further purified by the recrystallization procedure described above to give 0.58 g of **3** as a white solid (5%). MP: 36.0-36.5°C. IR (KBr) 2925.5, 1727.9, 1427.1, 1353.8, 1114.7, 1006.7, 948.8, 844.7, 607.5 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01 (s, 1H), 2.40 (s, 6H), 2.17 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.5, 193.2, 145.2, 137.9, 129.4, 126.0, 29.9, 14.9. HRMS calcd. for $C_9H_{10}O_3S_3$ 245.98429. Found 245.984844 (Error = 0.3 ppm).

***S,S'*-3,4-Dimethylthiophene-2,5-diyl diethanethioate (4).**

S,S'-3,4-Dimethylthiophene-2,5-diyl diethanethioate **4** was prepared via General Method 1. 2,5-Dibromo-3,4-dimethyl-thiophene was prepared via bromination of 1.00 g of 3,4-dimethylthiophene (8.91 mmol) by 1.68 g of NBS (9.44 mmol) in 35 mL of dichloromethane to

afford the product in 94% yield. NBS had to be added slowly at 0°C to control the reaction, but was then warmed to room temperature for an hour. The precipitate was then filtered, solvent removed, and the crude solid passed through a flash column with hexanes. This method proved to be much simpler than literature methods and the product gave identical spectra.[3,4]

1.05 g of 2,5-dibromo-3,4-dimethylthiophene (3.89 mmol) was dissolved in 10 mL of ether. 3.1 mL of 2.5 M nBuLi (7.8 mmol) in hexanes in 10 mL of ether were added as described in the procedure for General Method 1. After 10 minutes at -78°C, 0.25 g of sulfur (7.80 mmol) were added to the dark orange solution, which immediately became light yellow. The reaction was held at -78°C for 40 minutes after which 0.6 mL of acetyl chloride (8.6 mmol) were added via syringe and the reaction was allowed to warm to room temperature overnight. After being subjected to standard workup conditions and chromatography on silica eluted with dichloromethane (R_f = 0.32) the solid was recrystallized from hexanes to give 0.12 g of long lemon-white needles **4** (12%). MP: 79.5-80.0°C. IR (KBr) 1710.6, 1432.9, 1355.7, 1118.5, 952.7, 609.4 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 2.39 (s, 6H), 2.11 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.4, 145.0, 124.3, 29.8, 14.5. HRMS calcd. for $C_{10}H_{12}O_2S_3$ 259.99994. Found 260.000281 (Error = 0.5 ppm).

***S,S'*-2,5-Dimethylthiophene-3,4-diyl diethanethioate (5).**

S,S'-2,5-Dimethylthiophene-3,4-diyl diethanethioate **5** was prepared via General Method 1 from 3,4-dibromo-2,5-dimethyl-thiophene. 2,5-Dimethyl-thiophene was brominated according to the procedure outlined above for 2,5-dibromo-3,4-dimethyl-thiophene. This method again proved to be superior to the other known methods, which gave large amounts of tri- and tetrabrominated products.[6,7]

3.00 g of 3,4-dibromo-2,5-dimethyl-thiophene (11.1 mmol) were added drop wise to 9.3 mL of 2.5 M nBuLi (23.3 mmol) in hexanes in 50 mL of ether as described in General Method 1. The yellow solution slowly turned white and after 30 minutes at -78°C, 0.71 g of sulfur (22.1 mmol) were added. The reaction was held at -50°C for 60 minutes after which 2.4 mL of acetyl chloride (33.3 mmol) were added via syringe and the reaction was allowed to warm to room temperature overnight during which the reaction became white and formed large amounts of precipitate. After being subjected to standard workup conditions and chromatography on silica eluted with dichloromethane (R_f = 0.42) the solid was recrystallized from hexanes to give 0.20 g of off-white powder (12%). MP: 79.0-80.0°C. IR (KBr) 2362.38, 1708.6, 1386.57, 1128.16, 964.2, 676.9, 619.0 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 2.39 (s, 6H), 2.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 142.9, 123.8, 30.0, 15.1. HRMS calcd. for $C_{10}H_{12}O_2S_3$ 259.99994. Found 260.000537 (Error = 0.5 ppm).

***S,S'*-3-Methoxythiophene-2,5-diyl diethanethioate (6) and *S*-3-Methoxythiophen-2-yl ethanethioate (11).**

1.00 g of 2,5-dibromo-3-methoxythiophene (3.68 mmol), 2.9 mL of 2.5 M BuLi (7.4 mmol), 0.24 g of sulfur (7.48 mmol), and 0.8 mL of acetyl chloride (11.0 mmol) were combined according to General Method 1. After the standard workup chromatography on silica gel with a mixture of dichloromethane:hexanes (1:3 volume ratio) increasing to 1:0 eluted a small amount of the mono-substituted product first (R_f = 0.3) followed by the disubstituted product (R_f = 0.15) both as orange oils (0.10 g, 10%) requiring no further purification. IR (KBr) 3430.76, 2927.4, 2858.0, 1726.0, 1535.1, 1367.3, 1114.7, 952.7, 609.4 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.95 (s, 1H), 3.86 (s, 3H), 2.41 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7, 193.0, 159.8,

129.3, 123.3, 107.3, 59.2, 29.9, 29.6. HRMS calcd. for $C_9H_{10}O_3S_3$ 261.97920. Found 261.979448 (Error = 0.9 ppm).

By replacing THF with diethyl ether and following the General Method 3, **11** could be isolated in low yield with no **6** detected. Both methods gave small amounts of the other two isomers, which were isolated and characterized by ^{1}HNMR. Analysis of the splitting allowed each isomer to be assigned. IR (KBr) 2859.9, 2360.5, 1716.3, 1535.1, 1459.9, 1384.6, 1251.6, 1110.8, 1068.4, 948.9, 729.0, 609.4 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, J = 5.5 Hz, 1H), 6.85 (d, J = 5.5 Hz, 1H), 3.97 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 160.7, 130.1, 113.2, 110.1, 59.3, 29.6. HRMS calcd. for $C_7H_8O_2S_2$ 187.99657. Found 187.997657 (Error = 0.1 ppm).

***S,S'*-3-Acetylthiophene-2,5-diyl diethanethioate (7).**

S,S'-3-Acetylthiophene-2,5-diyl diethanethioate **7** was made by General Method 2. To 2.76 g of 2,3,5-tribromothiophene (8.55 mmol) in 100 mL of ether were added 3.4 mL of 2.5 M nBuLi (8.6 mmol) in hexanes as described above. After 30 minutes at -78°C, 0.27 g of sulfur (8.42 mmol) was added to the pale yellow solution which was allowed to warm to room temperature for an hour. After cooling to -78°C this procedure was repeated with another 3.4 mL of 2.5 M nBuLi (8.6 mmol) followed with 0.27 g of sulfur (8.42 mmol), and the mixture was allowed to stir for an hour at room temperature. After cooling to -78°C a third equivalent of 3.4 mL of 2.5 M nBuLi was added and after an hour, 6.1 mL of acetyl chloride (85.5 mmol) were added after which the reaction was allowed to warm to room temperature overnight. The reaction was then subjected to the standard workup followed by chromatography on silica gel with a mixture of dichloromethane:hexanes (1:1 volume ratio) increasing to 1:0. The crude solid was dissolved in dichloromethane and slowly dropped into a cold solution of hexanes. The precipitate

was filtered to give 0.09 g of **7** (4%) as a brown solid. MP: 131.5-133.0°C. IR (KBr) 3436.5, 2360.5, 1704.8, 1662.3, 1502.3, 1392.4, 1357.6, 1226.5, 1116.5, 958.5, 858.2, 640.3, 609.4 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (s, 1H), 2.504 (s, 3H), 2.498 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.0, 192.8, 192.6, 140.8, 139.0, 135.1, 127.7, 30.4, 30.0, 29.4. HRMS calcd. for $C_{10}H_{10}O_3S_3$ 273.97920. Found 273.979460 (Error = 0.8 ppm).

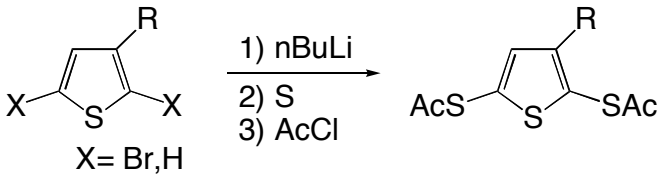
***S,S'*-3-Bromothiophene-2,5-diyl diethanethioate (8).**

S,S'-3-Bromothiophene-2,5-diyl diethanethioate **8** was prepared via General Method 2. To 7.79 g of 2,3,5-tribromothiophene (24.1 mmol) in 100 mL of ether were added 9.7 mL of 2.5 M nBuLi (24.1 mmol) in hexanes. Following the same procedure described in General Method 2 and in the synthesis of **7**, 0.77 g of sulfur (24.1 mmol) were then added and stirred at room temperature for an hour. This was repeated once and followed by 3.8 mL of acetyl chloride (53.1 mmol) as described. After being allowed to warm to room temperature overnight, the reaction was subjected to the standard workup followed by chromatography with hexanes then dichloromethane (R_f = 0.64). The crude product was dissolved in hot dichloromethane and hexanes, which upon cooling afforded a white solid that was decanted away from an orange oil. Cooling in an ice bath afforded 0.62 g of **8** lemon yellow needles (9%). MP: 60.5-61.0°C. IR (KBr) 3438.5, 2414.45, 1720.2, 1670.1, 1355.7, 1112.7, 945.6, 607.5 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (s, 1H), 2.44 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 191.3, 137.2, 131.7, 128.4, 119.2, 30.03, 30.00. HRMS calcd. for $C_8H_7BrO_2S_3$ 309.87915. Found 309.879522 (Error = 1.2 ppm).

The synthesis of the family of dimercaptothiophenes proceeded via one of three general methods as described above, the success of which were all highly solvent dependent. Initial attempts to utilize lithiation of the 2,5-dibromothiophene derivatives in tetrahydrofuran (THF)

(Method 1) were unsuccesful as were all attempts via Grignard[9] reagents. These reactions resulted only in small amounts of unreacted starting material and unidentifiable gums. It was, however, successful when alternating additions of butyllithium and sulfur were employed with ether as the solvent.[10,11]

In the cases where lithiation of the dibromothiophenes failed, 2,5-dihydrothiophenes were used. Attempts to follow the procedure of Chadwick and Willbe[12] were unsuccessful or resulted in very low yields of impure, black, highly viscous oils. This procedure, which calls for refluxing the thiophene derivative, TMEDA, and nBuLi in hexanes may be too harsh.[13,14] Instead, the use of a milder procedure proved to be much more successful.[15] The thiophene derivatives were readily dilithiated in ether at room temperature resulting in higher yields and easier purification. The procedure, however, failed in the case of 3-methoxythiophene, in which case it yielded only the mono-thioacetate. While yields were generally low, most of the starting materials could be easily accessed or were commercially available, permitting the one step procedure to be performed on the required scale.



In the case of the acetyl-functionalized compound **7**, the nature of the functional group required that it be incorporated subsequent to any lithiation procedures. In order to obtain **7**, a third equivalent of nBuLi was used in the procedure outlined by Method 2 starting from 2,3,5-tribromothiophene. Previous literature examples have shown that this lithiation is done

selectively allowing the first two substitutions to take place at the 2,5-positions followed by reaction at the 3-position which upon quenching with acetyl chloride yields **7**.[16]

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Figures of CVs Obtained from Electrochemical Characterization of the TBT Family Studied

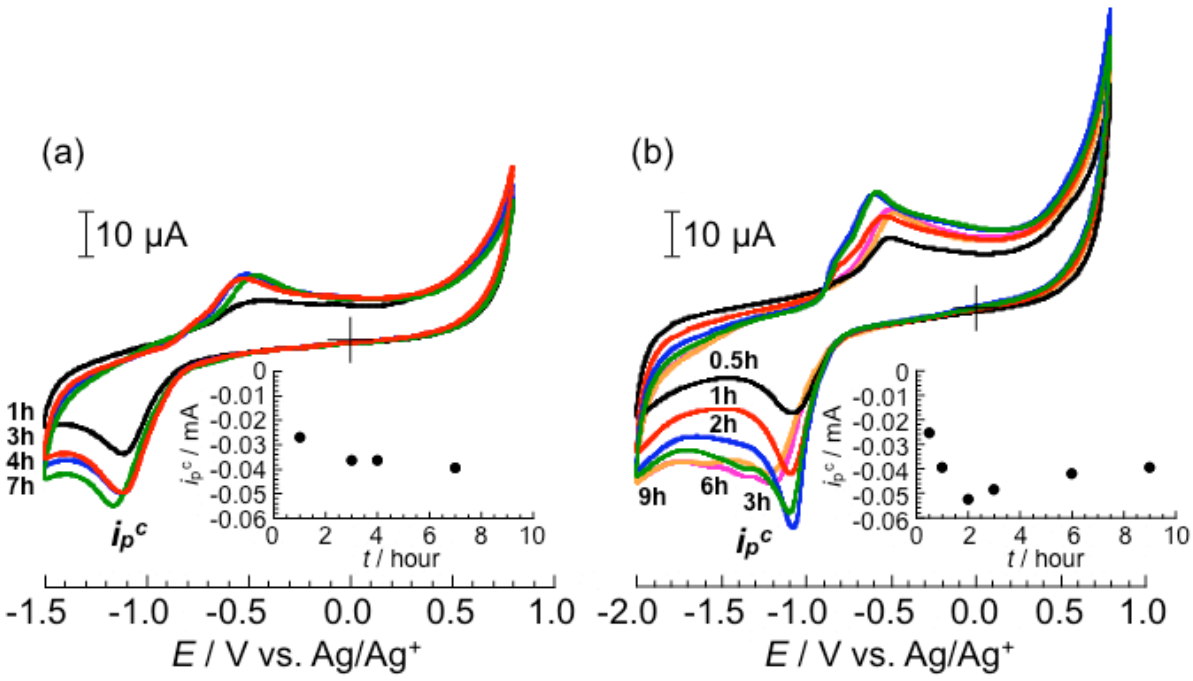

Figure S1. CVs for 1 mM TBT **1** at bare GCEs in 0.1 M $LiClO_4$/AN containing 50 mM NH_4OH. The CVs were obtained in the potential range (a) from -1.50 to +0.80 V and (b) from -2.00 to +0.80 V vs Ag/Ag^+. Scan rate was 200 mV s^{-1}. Each CV was repeated over varying time intervals (as indicated). Note that the largest peak change was observed between ~2-4 hours, and in (b) after ~6 hours, degradation appears to occur. Insets represent reduction peak current observed as a function of time.

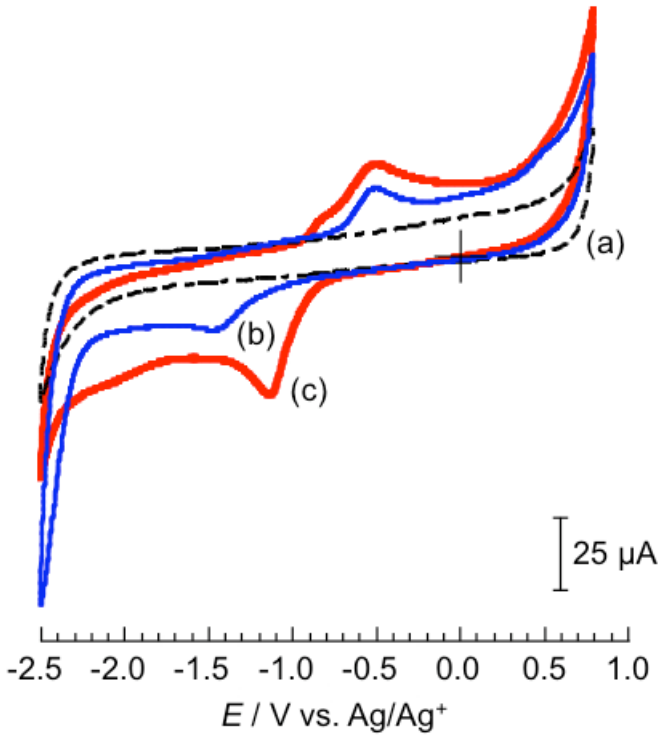

Figure S2. (a) CV for 50 mM NH_4OH at a bare GCE in 0.1 M $LiClO_4$/AN. CVs for 1 mM (b) TT **10** and (c) TBT **1** at bare GCEs in 0.1 M $LiClO_4$/AN containing 50 mM NH_4OH. The scan rate in all cases was 20 mV s^{-1}.

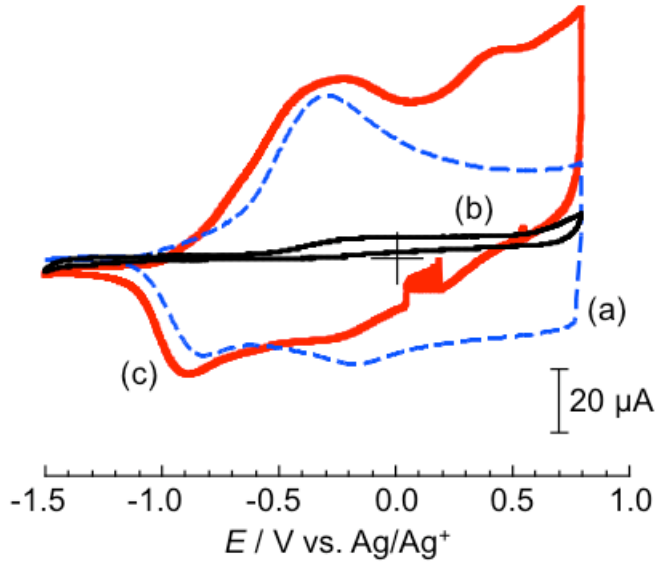

Figure S3. (a) CV for a PEDOT film-coated GCE in 0.1 M $LiClO_4$/AN. Representative CVs for 1 mM 3,4-TBT **2** at (b) bare and (c) PEDOT film-coated GCEs in 0.1 M $LiClO_4$/AN containing 50 mM NH_4OH. The scan rate in all cases was 20 mV s^{-1}.

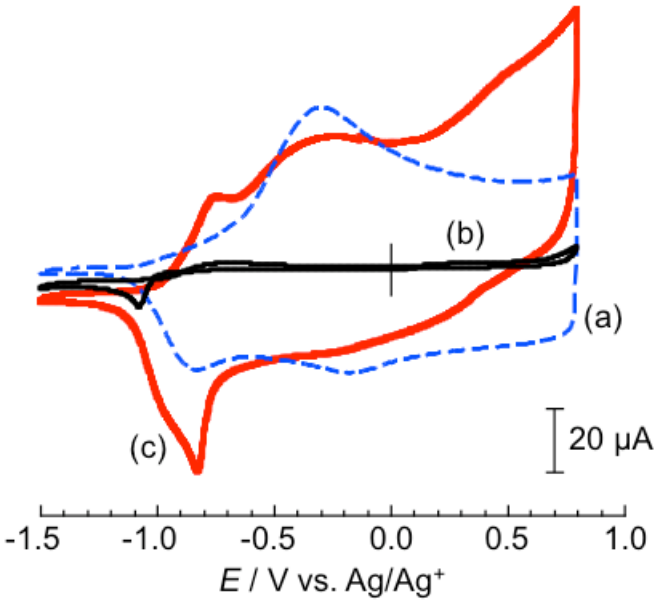

Figure S4. (a) CV for a PEDOT film-coated GCE in 0.1 M $LiClO_4$/AN. Representative CVs for 1 mM 3,4-dimethyl-TBT **4** at (b) bare and (c) PEDOT film-coated GCEs in 0.1 M $LiClO_4$/AN containing 50 mM NH_4OH. The scan rate in all cases was 20 mV s^{-1}.

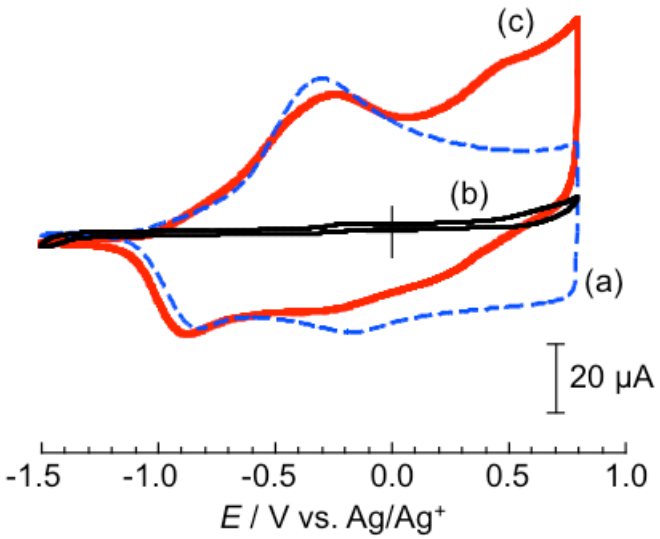

Figure S5. (a) CV for a PEDOT film-coated GCE in 0.1 M $LiClO_4$/AN. Representative CVs for 1 mM 2,5-dimethyl-TBT **5** at (b) bare and (c) PEDOT film-coated GCEs in 0.1 M $LiClO_4$/AN containing 50 mM NH_4OH. The scan rate in all cases was 20 mV s^{-1}.

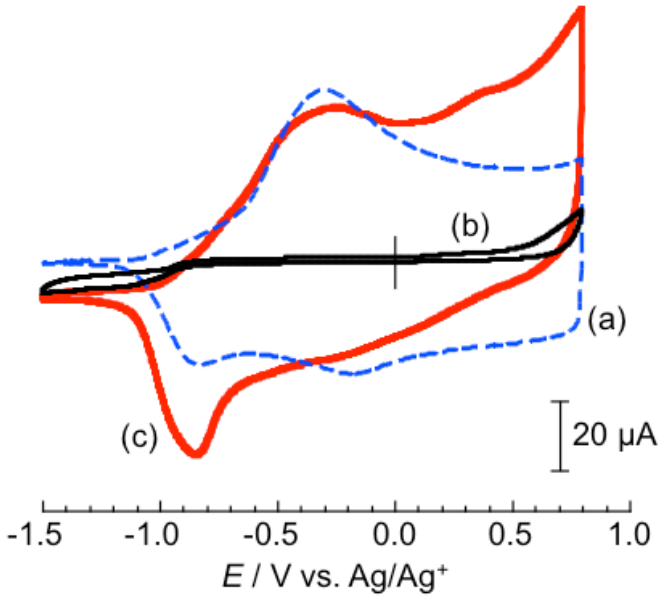

Figure S6. (a) CV for a PEDOT film-coated GCE in 0.1 M $LiClO_4$/AN. Representative CVs for 1 mM methoxy-TBT **6** at (b) bare and (c) PEDOT film-coated GCEs in 0.1 M $LiClO_4$/AN containing 50 mM NH_4OH. The scan rate in all cases was 20 mV s^{-1}.

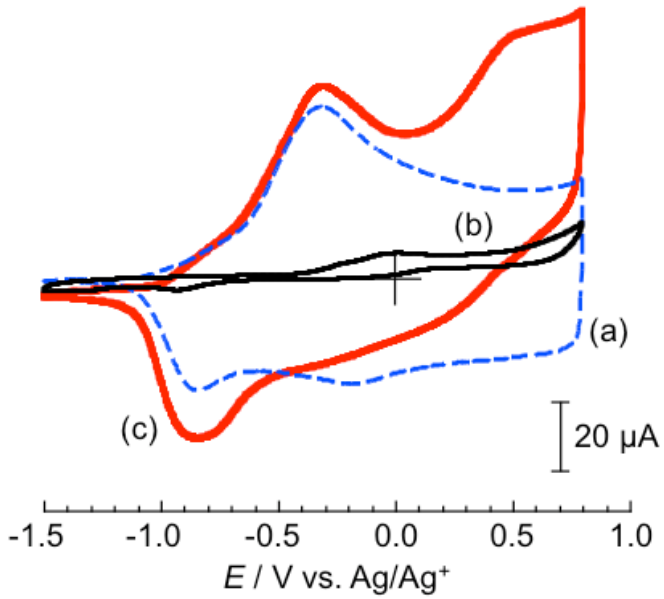

Figure S7. (a) CV for a PEDOT film-coated GCE in 0.1 M $LiClO_4$/AN. Representative CVs for 1 mM acetyl-TBT **7** at (b) bare and (c) PEDOT film-coated GCEs in 0.1 M $LiClO_4$/AN containing 50 mM NH_4OH. The scan rate in all cases was 20 mV s^{-1}.

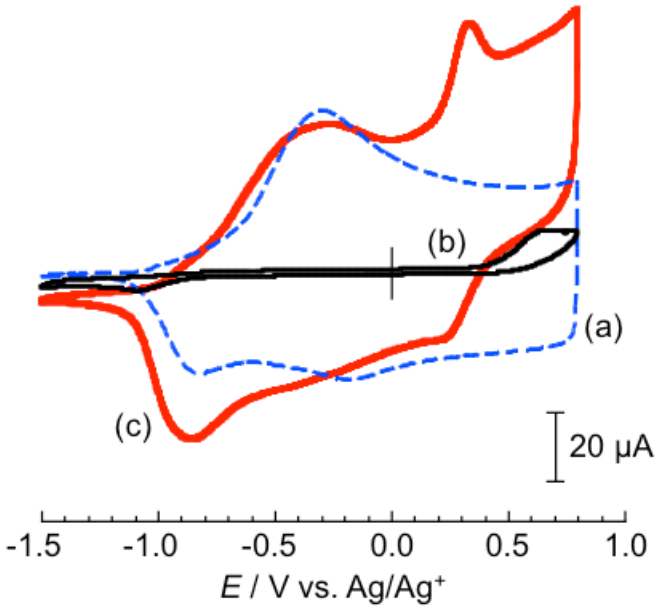

Figure S8. (a) CV for a PEDOT film-coated GCE in 0.1 M $LiClO_4$/AN. Representative CVs for 1 mM bromo-TBT **8** at (b) bare and (c) PEDOT film-coated GCEs in 0.1 M $LiClO_4$/AN containing 50 mM NH_4OH. The scan rate in all cases was 20 mV s^{-1}.

Figures of Profile for a PEDOT Film Cast on Indium Tin Oxide (ITO) Electrodes, and Plots of PEDOT Film Thickness as a Function of Charge Consumed during the Electrochemical Polymerization of EDOT.

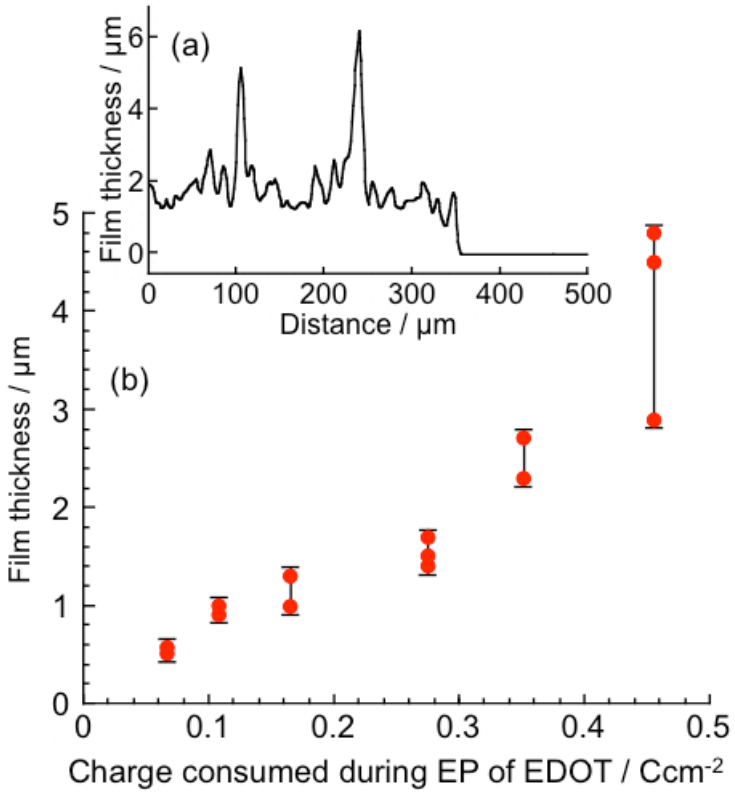

Figure S9. (a) Profile for a PEDOT film cast on ITO electrodes. PEDOT films were prepared on ITO electrodes via electrochemical polymerization of EDOT in a 0.1 M $LiClO_4$/AN solution containing 20 mM EDOT. (b) PEDOT film thickness as a function of charge consumed during the electrochemical polymerization (EP) of EDOT. Note that the measured charge density is directly correlated with film thickness, although significant film-to-film variation in thickness exists due to the rough surface profile.