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Synthesis of thiol substituted oligoanilines for molecular device candidates☆

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Abstract—The synthesis of thioacetate derivatized oligoanilines designed for molecular electronic device purposes is described. Reversible oxidation between the non-conductive leuco base and conductive emeraldine salt forms of these compounds may produce switching effects and device behavior. The targeted compounds contain a sulfur moiety as a means to connect the molecules to metallic electrodes.

Increasing costs and physical barriers attributed with silicon based solid-state computing technology have given way to substantial work in the field of molecular electronics.[1–3] It has been shown that single molecules can undergo reversible switching behavior in solid-state testbeds.[4] We have designed and synthesized oligoaniline-based molecules as a new class of potential switching and memory type devices. Oligoanilines offer the possibility to reversibly oxidize between different conductivity states in a controlled fashion,[5] namely between the non-conductive leuco base and the conductive emeraldine salt giving rise to a potential on–off 'memory-like' effect.

Extensive research on couplings of aryl halides with anilines by Buchwald and Hartwig[6,7] has facilitated the synthesis of oligoanilines. We introduce a new series of oligoanilines for use as potential molecular electronic devices by incorporating a sulfur moiety into the molecule, which allows contact between the molecule and a metal electrode. We also synthesized oligomers with methylated nitrogen atoms to ensure oxidation only to the highly conductive emeraldine salt and not to the non-conductive emeraldine base or leuco salt, provided pH is controlled.[8] Additionally, each nitrogen atom is capable of losing one electron, therefore the structures here could offer multiple independent electronic states. The structures of the oligoaniline targets (**1**–**5**) are shown in Figure 1.

The synthesis of oligomer **1** is shown in Scheme 1. Employing Buchwald's conditions,[6] *N*-phenyl-*p*-phenylenediamine was coupled to 2-(trimethylsilyl)ethyl-4′-bromophenyl sulfide,[9] to afford **6**. Due to the harsh coupling conditions, the robust ethyltrimethylsilyl protecting group was employed rather

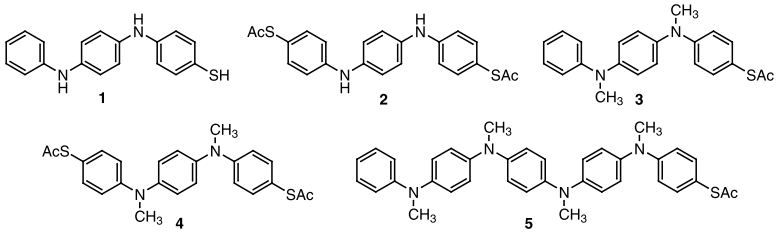

Figure 1. Oligoaniline targets for device assembly and testing.

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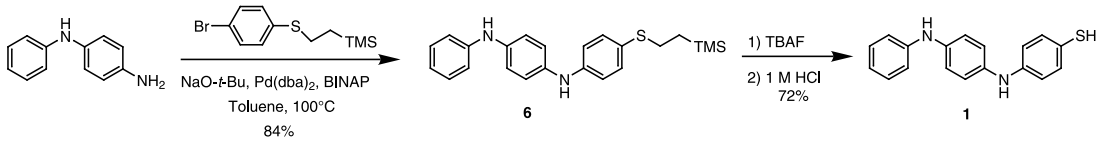


Scheme 1. Synthesis of the monothiol oligoaniline dimer **1**.

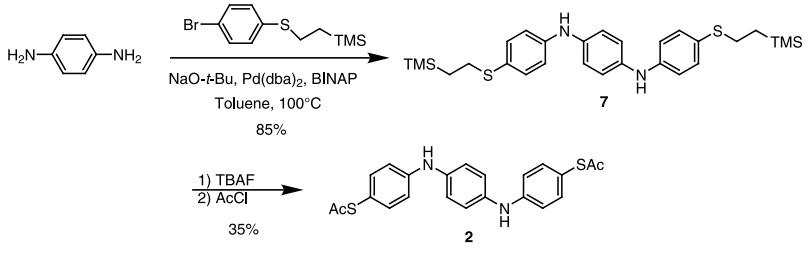
than the more labile thioacetate. Deprotection of the ethyltrimethylsilyl group using tetrabutylammonium fluoride[9] and quenching with excess 1 M HCl afforded **1** as the free thiol.

The synthesis of oligoaniline **2** (Scheme 2) began by coupling *p*-phenylenediamine to 2-(trimethylsilyl)ethyl-4′-bromophenyl sulfide to afford the dicoupled product **7**. Deprotection of **7** using tetrabutylammonium fluoride followed by quenching with acetyl chloride afforded the dithioacetate oligoaniline dimer **2**. Attempts to quench the dithiolate with HCl in order to isolate the dithiol resulted in the formation of a poly(disulfide) mixture. However, quenching with acetyl chloride affords the dithioacetate which can be deprotected in situ and assembled on gold in a manner similar to that used for the monothiol.[10] Therefore, the thioacetate moieties provide a convenient handle for isolation, particularly when the targets are α,ω-difunctionalized, since the aromatic thiols are so prone to oxidative dimerization.

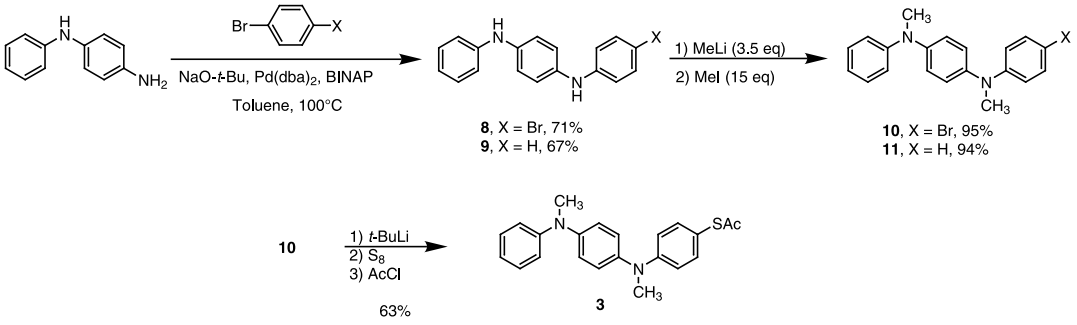
Our attempts to synthesize **3** via deprotection of an ethyltrimethylsilyl group proved ineffective, therefore we used an alternative route as shown in Scheme 3. Coupling *N*-phenyl-*p*-phenylenediamine with *p*-dibromobenzene afforded the desired product **8**. Treating **8** with methyllithium at −78°C followed by the addition of methyl iodide at −60°C afforded intermediate **10** in excellent yield. Reacting **10** with *tert*-butyllithium followed by the addition of sulfur and quenching with acetyl chloride afforded the target device **3**. We also synthesized the unfunctionalized oligoaniline dimer **9**[11] by coupling *N*-phenyl-*p*-phenylenediamine with bromobenzene, as well as the unfunctionalized *N*-methyl dimer **11**[12] by treating **9** with methyllithium and quenching with methyl iodide. **9** and **11** were needed for subsequent electrochemical characterization as models for surface-bound **3**.

The *N*,*N*′-dimethyl dithioacetate dimer **4** was synthesized in a similar fashion. As shown in Scheme 4, *p*-phenylenediamine was coupled to *p*-dibromobenzene to afford the dicoupled product **12**.[13] Treating **12** with methyllithium followed by methyl iodide afforded the dibromo species **13**. Reacting **13** with *tert*-butyllithium at −78°C followed by the addition of sulfur and quenching with acetyl chloride gave **4**.

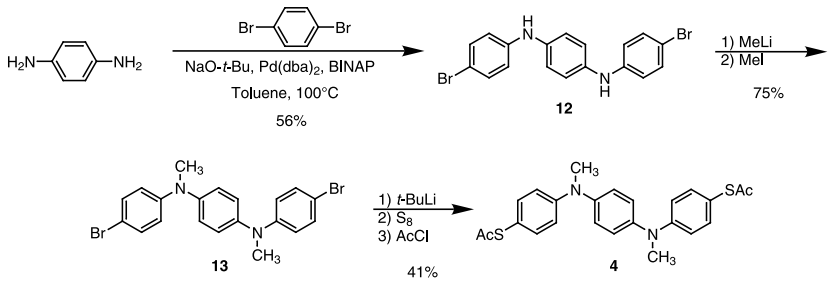
The synthesis of the tetramer **5** (Scheme 5) was accomplished by coupling the dibromide **13** with *N*-phenyl-*p*-phenylenediamine which afforded the monocoupled intermediate. Reacting immediately (to avoid air oxidation to the diiminoquinone) with methyllithium followed by methyl iodide, yielded the monobromo tetramer **14**. Treating **14** with *tert*-butyllithium, then sulfur and acetyl chloride afforded the target com-



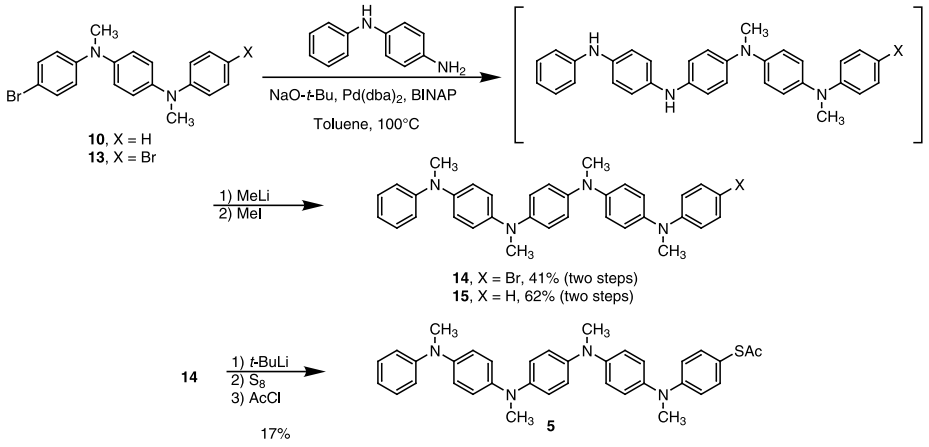
Scheme 2. Synthesis of the dithioacetate oligoaniline **2**.



Scheme 3. Synthesis of *N*-methyl oligoaniline dimers.



Scheme 4. Synthesis of the dithioacetate oligoaniline dimer **4**.



Scheme 5. Synthesis of the monothioacetate oligoaniline tetramer **5** and unfunctionalized tetramer **15**.

pound **5**, albeit in low yield. For electrochemical characterization, we also synthesized the unfunctionalized *N*-methyl tetramer **15** by coupling **10** with *N*-phenyl-*p*-phenylenediamine, followed by treatment with methyllithium and methyl iodide.

We plan to assess the compounds synthesized[14] in this work in several testbeds, including the nanopore and planar devices,[15] as well as the cross wire test structure.[16] These results will be reported separately.

Acknowledgements

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14. Selected characterization data. **1**: Mp: 151–160°C. IR (KBr) 3397.99, 3019.09, 2399.90, 1596.86, 1514.52, 1424.96, 1215.54 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (m, 4H), 7.05 (m, 6H), 6.90 (m, 3H), 5.63 (s, 1H), 5.59 (s, 1H), 3.41 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 143.9, 138.0, 137.0, 133.0, 129.8, 121.7, 121.1, 120.6, 118.7, 117.3, 117.0. HRMS calcd for $C_{18}H_{16}N_2S$: 292.1034. Found: 292.1033. **2**: Mp: 198–200°C. IR (KBr) 3428.85, 3019.22, 2400.00, 1699.20, 1595.12, 1514.21, 1424.26, 1215.46 cm^{-1}. ^1H NMR (400 MHz, $(CD_3)_2CO$) δ 7.59 (s, 2H), 7.22 (d, $J=8.3$ Hz, 4H), 7.20 (s, 4H), 7.07 (d, $J=8.3$ Hz, 4H), 2.35 (s, 6H). ^{13}C NMR (100 MHz,

$(CD_3)_2CO$) δ 195.4, 147.5, 137.7, 136.8, 122.2, 116.9, 116.2, 29.8. HRMS calcd for $C_{22}H_{20}N_2O_2S_2$: 408.0966. Found: 408.0961. **3**: Mp: 104–106°C. IR (KBr) 3018.03, 2943.21, 2882.87, 2815.66, 2400.24, 1696.27, 1593.38, 1496.63, 1338.79, 1255.20, 1215.80, 1190.46, 1131.55 cm^{-1}. ^1H NMR (400 MHz, $(CD_3)_2CO$) δ 7.29 (m, 2H), 7.19 (d, $J=9.1$ Hz, 2H), 7.14 (d, $J=9.1$ Hz, 2H), 7.06 (m, 4H), 6.95 (t, $J=7.1$ Hz, 1H), 6.81 (d, $J=9.1$ Hz, 2H), 3.33 (s, 3H), 3.31 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 196.6, 150.8, 149.4, 146.5, 141.8, 135.9, 129.7, 127.0, 121.9, 121.8, 120.8, 115.8, 115.1, 40.8, 40.7, 30.3. HRMS calcd for $C_{22}H_{22}N_2OS$: 362.1454. Found: 3623.1453. **4**: Mp: 168–170°C. IR (KBr) 3018.40, 2884.21, 2816.94, 2400.23, 1887.47, 1693.94, 1591.40, 1556.23, 1495.02, 1453.60, 1423.00, 1337.34, 1254.98, 1216.42, 1190.52, 1120.45, 1074.64 cm^{-1}. ^1H NMR (400 MHz, $(CD_3)_2CO$) δ 7.23 (m, 8H), 6.92 (d, $J=8.9$ Hz, 4H), 3.36 (s, 6H), 2.35 (s, 6H). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 194.7, 150.6, 144.8, 136.0, 126.1, 116.8, 116.7, 40.1, 29.3. HRMS calcd for $C_{24}H_{24}N_2O_2S_2$: 436.1279. Found: 436.1275. **5**: Mp: 148–152°C. IR (KBr) 3018.89, 2399.90, 1693.59, 1593.26, 1498.93, 1423.92, 1333.27, 1215.92, 1133.39 cm^{-1}. ^1H NMR (400 MHz, $(CD_3)_2CO$) δ 7.19 (m, 4H), 7.05 (m, 10H), 6.93 (d, $J=8.7$ Hz, 2H), 6.89 (m, 2H), 6.8 (t, $J=6.9$ Hz, 1H), 6.75 (d, $J=8.7$ Hz, 2H), 3.30 (m, 6H), 3.28 (s, 3H), 3.27 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, THF-d_8) δ 194.6, 151.7, 150.7, 148.3, 146.1, 145.8, 144.0, 143.5, 140.7, 136.2, 129.6, 127.7, 125.0, 124.8, 122.3, 121.8, 120.0, 119.1, 118.3, 115.9, 115.4, 40.8, 40.6, 40.6, 29.5. HRMS calcd for $C_{36}H_{36}N_4OS$: 572.2610. Found: 572.2600. **15** Mp: 208–210°C. IR (KBr) 3019.23, 2400.21, 1596.94, 1503.67, 1332.57, 1216.19, 1133.53 cm^{-1}. ^1H NMR (500 MHz, THF-d_8) δ 7.12 (t, $J=9.9$ Hz, 4H), 6.96 (m, 8H), 6.89 (d, $J=9.9$ Hz, 4H), 6.81 (d, $J=9.9$ Hz, 4H), 6.72 (t, $J=9.9$ Hz, 2H), 3.25 (s, 6H), 3.23 (s, 6H). ^{13}C NMR (100 MHz, THF-d_8) δ 148.3, 143.9, 142.3, 140.7, 127.1, 122.9, 120.5, 118.5, 117.1, 115.2, 38.4, 38.1. HRMS calcd for $C_{34}H_{34}N_4$: 498.2783. Found: 498.2791.

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