

# Substituted oligoanilines: synthesis and characterization

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Received 23 January 2004; received in revised form 1 June 2004; accepted 13 June 2004

Available online 31 July 2004

## Abstract

Substituted trimeric oligoanilines were synthesized by palladium-catalyzed aromatic amination, followed by hydrogenolysis or transamination and thermolysis. The effects of substituent groups on the electronic and electrochemical properties were characterized by cyclic voltammetry and UV–vis spectroscopy. Electron-donating groups decreased the oxidation potential and had little effect on the UV–vis absorption, while electron-withdrawing groups increased the oxidation potential and the UV–vis absorption wavelengths. Electrical conductivities were in the range from  $10^{-5}$  to  $10^{-3}$  S/cm when the oligoanilines were doped with iodine.

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*Keywords:* Substituted oligoanilines; Palladium-catalyzed aromatic amination; NMR spectroscopy; UV–vis spectroscopy; Cyclic voltammetry; Conductivity

## 1. Introduction

In the last few years, there has been a growing interest in the synthesis and characterization of oligoanilines. These oligomers first served as model compounds to rationalize and predict the properties of high molecular weight, intractable and ill-defined polyaniline [1]. The structures of polyaniline are very complicated. Polyaniline can exist in different oxidation states (leucoemeraldine, emeraldine and pernigraniline) and different isomeric structures (positional, geometrical and conformational isomers). These structures have significant effects on the electronic and optical properties of the polymers. Epstein and co-workers found that only a small fraction of charge carriers in polyaniline contributed to the observed conductivity ( $\sim 100$  S/cm) [2]. If all charge carriers participated in the conduction, polyaniline should have a conductivity similar to that of copper. They believed that the imperfections in the polymer structures might be the cause for the low conductivity. To study the structure–property relationships of polyaniline, the oligomer approach has been applied because of its well-defined structures, processibility

and ease of characterization. In addition to serving as model compounds, oligoanilines also find their own applications, e.g., corrosion protection [3] and field effect transistors [4].

Incorporation of conjugated oligomers into polymer structures combines the properties of the specific oligomer and desired polymer properties such as mechanical strength and film forming properties. Oligoanilines can be incorporated into polymer main chains as well as side chains [5–7]. Our research interest is to synthesize and study poly(acrylate)s and poly(acrylamide)s containing oligoanilines as side chains. Several polymers have been made and characterized in our lab [8–11]. The synthesis of amino-capped oligoanilines has been reported; however, there are few studies on the properties of other substituted oligomers. Here, we report the synthesis of substituted trimeric anilines by palladium-catalyzed aromatic amination. These trimers were characterized by nuclear magnetic resonance spectroscopy, cyclic voltammetry and UV–vis spectroscopy. The substituent effects on the electronic state and electrochemistry were also investigated. For comparison, the properties of the dimeric aniline, *N*-phenyl-1,4-benzenediamine (PBD) and the tetrameric aniline, *N*-(4-aminophenyl)-*N'*-(4-anilinophenyl)-1,4-benzenediamine (APAPBD), are also reported in this paper.

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## 2. Experimental

### 2.1. Materials

All chemicals were purchased from ACROS Organics. Bis[(2-diphenylphosphino)phenyl] ether (DPEphos) and *N*-(diphenylmethylene)-*N'*-(*tert*-butoxycarbonyl)-*N'*-(4-bromophenyl)-1,4-benzenediamine (**1**) were synthesized according to literature methods [10,12]. The synthesis of tetrameric aniline, *N*-(4-aminophenyl)-*N'*-(4-anilinophenyl)-1,4-benzenediamine, was described previously [10]. Toluene and tetrahydrofuran were refluxed in sodium metal for 24 h followed by distillation under argon.

### 2.2. Characterization

Melting points were measured by a capillary melting point apparatus without calibration. Proton NMR spectra were recorded on a Varian 500 spectrometer using solvent residues as references. MALDI-TOF MS was applied to measure the molecular mass of the oligoanilines using 2,5-dihydroxybenzoic acid as a matrix. UV-vis spectra were recorded on a Perkin-Elmer Lambda 4C UV-vis spectrophotometer. FTIR spectra were recorded using a BioRad Excaliber FTS3000. Elemental analysis was performed by Midwest Microlabs. Cyclic voltammetry was conducted on a Zahner IM6e electrochemical station with a three-electrode cell using Pt disc, Pt wire and Ag/AgCl (3.0 M NaCl) as the working, counter and reference electrodes, respectively. Tetrabutylammonium perchlorate acetonitrile solution (0.1 M) was used as the supporting electrolyte. The scan rate was 100 mV/s. Electrical conductivity was measured by the four-point probe method.

### 2.3. Synthesis

#### 2.3.1. *N*-(4-aminophenyl)-*N'*-phenyl-1,4-benzenediamine (APPBD) (**2a**)

Compound **1** (2.00 g, 3.79 mmol), palladium acetate (20 mg,  $8.9 \times 10^{-2}$  mmol) and DPEphos (61 mg,  $1.1 \times 10^{-1}$  mmol) were charged into a flask and purged with argon. Aniline (0.42 g, 4.5 mmol) was added, followed by toluene (20 mL). Sodium *tert*-butoxide (0.51 g, 5.3 mmol) was added in one portion. The reaction mixture was heated at 110 °C with stirring for 24 h. The solvent was removed by rotary evaporation. The residue was dissolved in dichloromethane, washed with distilled water, dried over anhydrous sodium sulfate, and concentrated. The product was separated by column chromatography (silica gel, ethyl acetate/hexanes). This compound (1.00 g, 1.85 mmol), ammonium formate (1.75 g, 27.8 mmol) and palladium on carbon (5%, 0.20 g,  $9.4 \times 10^{-2}$  mmol Pd) were charged into a round bottom flask and purged with argon. Tetrahydrofuran (10 mL) and methanol (25 mL) were added. The reaction mixture was refluxed for 24 h. The solution was concentrated and the residue was dissolved in dichloromethane and filtered through Celite and

concentrated. The solid was ground and washed with hexanes and then filtered. The white powder was dried in vacuo at 50 °C for 24 h. The powder was heated at 180 °C in a Schlenk tube under argon for 10 h. Product: off-white granules; mp: 148–150 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 7.64 (s, 1H), 7.26 (s, 1H), 7.12 (t, 2H), 6.92 (d, 2H), 6.85 (d, 2H), 6.81–6.78 (m, 4H), 6.64 (t, 1H), 6.52 (d, 2H), 4.67 (s, 2H). MALDI-TOF MS (MW 275.4). IR (KBr, cm<sup>-1</sup>): 3381, 3024, 1597, 1514, 1302. Anal. Calcd. for C<sub>18</sub>H<sub>17</sub>N<sub>3</sub>: C, 78.52; H, 6.22; N, 15.26. Found: C, 78.14; H, 6.22; N, 14.96.

#### 2.3.2. *N*-(4-aminophenyl)-*N'*-(4-methoxyphenyl)-1,4-benzenediamine (APMBD) (**2b**)

APMBD was prepared in a manner similar to that described for APPBD above. Product: off-white granules; mp: 150–152 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 7.34 (s, 1H), 7.14 (s, 1H), 6.86–6.82 (m, 4H), 6.78–6.74 (m, 6H), 6.50 (d, 2H), 4.63 (s, 2H), 3.67 (s, 3H). MALDI-TOF MS (MW 305.4). IR (KBr, cm<sup>-1</sup>): 3389, 3028, 2931, 1613, 1513, 1238. Anal. Calcd. for C<sub>19</sub>H<sub>19</sub>N<sub>3</sub>O: C, 74.73; H, 6.27; N, 13.76. Found: C, 74.46; H, 5.84; N, 12.29.

#### 2.3.3. *N*-(4-aminophenyl)-*N'*-(4-cyanophenyl)-1,4-benzenediamine (APCBD) (**2c**)

APCBA was prepared in a manner similar to that described for APPBD. However, the diphenylmethylene group was removed by different method using hydroxylamine [13]. Product: off-white granules; mp: 179–181 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 8.50 (s, 1H), 7.49 (s, 2H), 7.47 (s, 1H), 6.96 (d, 2H), 6.84–6.80 (m, 6H), 6.54 (d, 2H), 4.76 (s, 2H). MALDI-TOF MS (MW 300.4). IR (KBr, cm<sup>-1</sup>): 3352, 3030, 2207, 1602, 1513, 1307. Anal. Calcd. for C<sub>19</sub>H<sub>16</sub>N<sub>4</sub>: C, 75.98; H, 5.37; N, 18.65. Found: C, 76.65; H, 5.38; N, 18.40.

## 3. Results and discussion

### 3.1. Synthesis of oligoanilines

Recently, palladium-catalyzed aromatic amination has emerged as a powerful method for the formation of C–N bonds. Oligoanilines with different chain lengths and functional groups were synthesized using this method [13]. In this work, palladium-catalyzed amination methodology was used to couple compound **1** and aniline as well as its derivatives (4-methoxyaniline and 4-cyanoaniline). In these experiments, palladium acetate (Pd(OAc)<sub>2</sub>) and DPEphos were used as catalyst and ligand and sodium *tert*-butoxide as a base. The reaction was carried out in toluene at 110 °C for 24 h. The synthetic route for substituted trimeric anilines is shown in Fig. 1. The yields of these reactions were fairly high, 93, 81 and 79% for the coupling with aniline, 4-methoxyaniline and 4-cyanoaniline, respectively. This indicated that the Pd(OAc)<sub>2</sub>/DPEphos system was highly efficient for the arylation of either electron-rich or electron-deficient aromatic amines. Two methods were applied to remove the

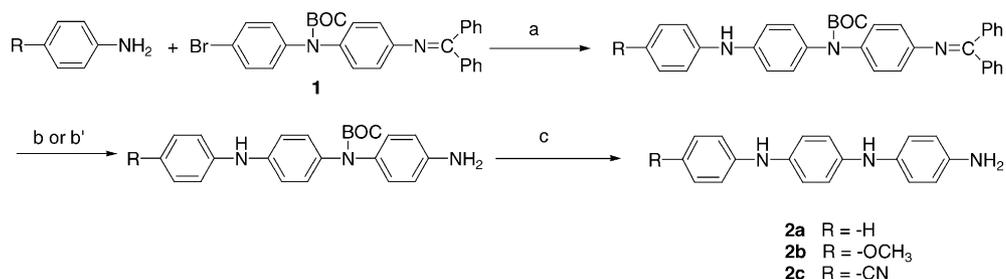


Fig. 1. Synthesis of substituted trimeric anilines. Key: (a) Pd(OAc)<sub>2</sub>, DPEphos, NaOt-Bu, toluene, 110 °C, 24 h; (b) R: -H, -OCH<sub>3</sub>: Pd/C, NH<sub>4</sub>HCO<sub>2</sub>, THF/MeOH, 60 °C, 24 h; (b') R: -CN: HONH<sub>2</sub>, pyridine, CHCl<sub>3</sub>/THF/EtOH, 3 h; (c) 180 °C, 10 h.

diphenylmethylene protective group. For trimer APPBD and trimer APMBD, palladium-catalyzed hydrogenolysis was used. However, the cyano group was partially reduced under the same reaction conditions. The alternative method was the treatment of the oligomers with hydroxylamine at room temperature. These two methods afforded products in 68–86% yields. The *tert*-butoxycarbonyl group was quantitatively removed by thermolysis in argon at 180 °C for 10 h. Tetrameric aniline APAPBD was prepared using similar procedure [10].

### 3.2. Nuclear magnetic resonance spectroscopy

Proton NMR spectroscopy was used to characterize and investigate the effect of the substituents at the opposite terminus of the amine-terminated oligoanilines. The spectra of dimer PBD, trimer APPBD and tetramer APAPBD have a resonance at 4.6 ppm, which is attributed to the primary amine group. Secondary amine resonances appeared at 7.5 ppm for

dimer PBD, 7.6 ppm and 7.3 ppm for trimer APPBD and 7.7, 7.4 and 7.1 ppm for tetramer APAPBD.

The chemical shifts of amine groups in the three trimers were quite different (Fig. 2). The resonance of the primary amine appeared at 4.67 ppm for APPBD, 4.63 ppm for APMBD and 4.76 ppm for APCBD. There was little effect on the primary amine resonance by the methoxy group. However, the cyano group significantly decreased the electron density of primary amine group and moved the resonance toward lower field. The resonances for the secondary amine groups were also affected by the substitution. In APPBD, the secondary amine signals appeared at 7.64 and 7.26 ppm. However, these resonances moved remarkably toward high field (7.34 and 7.14 ppm) in APMBD and low field (8.50 and 7.47 ppm) for APCBD. These results showed that the substituent effect of the cyano group was stronger than that of the methoxy group, and significant modification of the redox properties of the oligoanilines should be expected through end-group substituents.

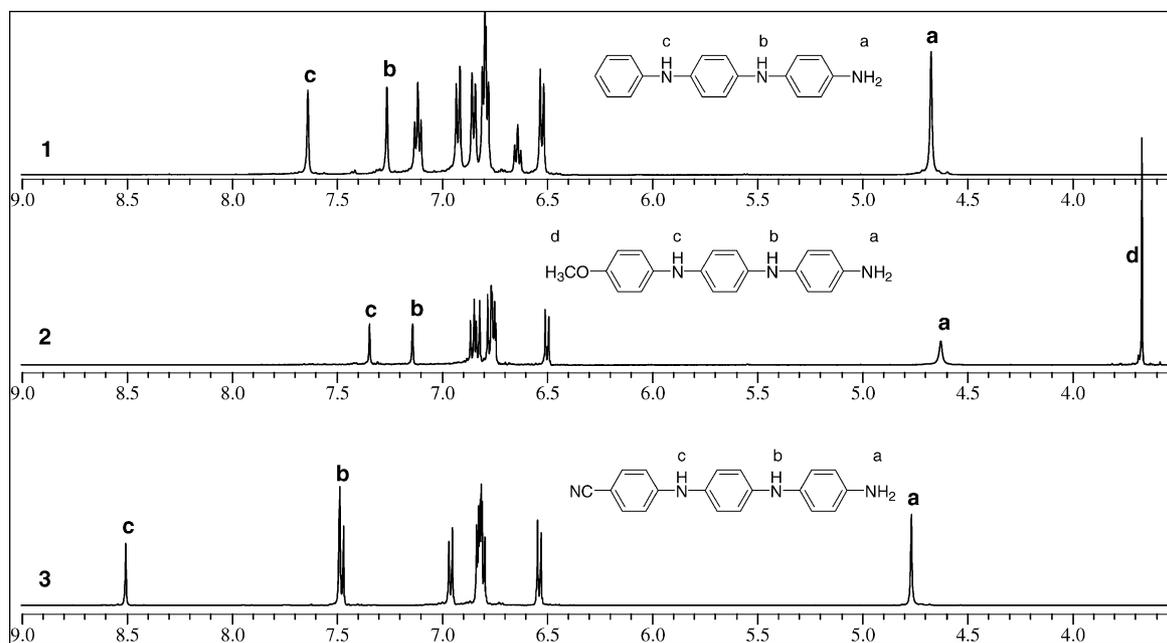


Fig. 2. Proton NMR of (1) APPBD; (2) APMBD; and (3) APCBD in DMSO-d<sub>6</sub>.

Table 1  
The UV–vis absorption and electrochemical properties of substituted trimers

|        | UV–vis (reduced, nm) | UV–vis (oxidized, nm) | Oxidation potential (V) | Conductivity (S/cm) |
|--------|----------------------|-----------------------|-------------------------|---------------------|
| PBD    | 291                  | 290, 427              | 0.45, 0.94              | $3 \times 10^{-6}$  |
| APBD   | 311                  | 304, 555              | 0.33, 0.67, 1.40        | $6 \times 10^{-3}$  |
| AMBD   | 311                  | 310, 554              | 0.29, 0.62, 1.25        | $2 \times 10^{-3}$  |
| ACBD   | 332                  | 329, 565              | 0.40, 0.76, 1.46        | $9 \times 10^{-5}$  |
| APAPBD | 323                  | 303, 577              | 0.27, 0.54, 0.90, 1.08  | $4 \times 10^{-2}$  |

### 3.3. UV–vis spectroscopy

The electronic structures of oligoanilines were studied by UV–vis spectroscopy (Table 1). In the reduced state of the various oligoanilines, only one absorption peak was observed at about 300 nm, which is due to the  $\pi$ – $\pi^*$  transition of benzenoid ring. The wavelength of maximum absorption  $\lambda_{\max}$  increased with chain length from 291 nm (dimer PBD) to 311 nm (trimer APPBD) and 323 nm (tetramer APAPBD). The maxima of the absorptions for APPBD and APMBD were 311 nm, while the absorption for APCBD appeared at a noticeably longer wavelength (332 nm). In a theoretical study of substituent effects of oligoanilines [14], Vaschetto and Re-tamal showed that electron-withdrawing groups (e.g., nitro and cyano) lowered the LUMO energy more than that of the HOMO, resulting in a decrease of  $\Delta E$  (HOMO–LUMO), i.e., a red-shift of absorption. Electron-donating groups (e.g., methyl and methoxy) had no or little effect on the absorption wavelength because of the weak interaction between the substituents and HOMO orbitals.

For all of the oligomers in Table 1, oxidation was performed by simply bubbling oxygen into their *N,N*-dimethylformamide (DMF) solutions. Two peaks appeared subsequently in all of the UV–vis spectra (Fig. 3). The first peak at about 300 nm ( $\pi$ – $\pi^*$  transition of the benzenoid ring) was shifted to slightly lower wavelength as compared to the

reduced states. The other peak is due to the charge transfer from the benzenoid ring to the quinoid ring. The wavelength increased with the chain length from 427 nm (dimer PBD) to 577 nm (tetramer APAPBD). The oxidative stability of substituted trimers varied with structure. The oligomers APPBD and APMBD were easily oxidized, showing a characteristic purple–blue color. Oligomer APCBD was difficult to oxidize and developed a blue color in solution after about one week. When silver (I) oxide was added, all solutions turned purple–blue within minutes.

### 3.4. Cyclic voltammetry

The electrochemistry of the oligomers was characterized by cyclic voltammetry. The experiments were conducted in a three-electrode cell, using Pt disc as a working electrode, Pt wire as a counter electrode and Ag/AgCl (3.0 M, NaCl) electrode as a reference electrode. The supporting electrolyte was tetrabutylammonium perchlorate acetonitrile solution (0.1 M). The concentration of oligomers was  $10^{-3}$  M. The oxidation potentials are summarized in Table 1. For all oligoanilines, the number of oxidation peaks was equal to the number of repeat phenyl rings in the oligomers, indicating that every unit in the oligomers could be oxidized. The first oxidation potential depended on the chain length of the oligomers. The potentials decreased from 0.45 V (dimer PBD) to 0.33 V (trimer APPBD) and 0.27 V (tetramer APAPBD). The trend in the ease of oxidation indicated that the stability of cation radicals generated in the oxidation increased with the chain length because of longer delocalization range.

All voltammograms for the substituted trimeric anilines were similar (Fig. 4). In the scan range from  $-0.2$  to  $1.0$  V, there are two oxidation peaks for all three compounds. When the CV was scanned to higher potential, e.g.,  $1.6$  V, a third oxidation peak was observed. However, significantly smaller reduction peaks were observed during the reverse sweep, indicating that the oxidation product was not stable and chemical reaction may have occurred at higher potentials. It is obvious from these experiments that the oxidation potential changes with the substitution. Trimer APPBD was oxidized at 0.33 and 0.67 V. Trimer APMBD was oxidized at 0.29 and 0.62 V while trimer APCBD was oxidized at 0.40 and 0.76 V. These results indicated that the electron-donating group lowered the oxidation potential while the strong electron-withdrawing group remarkably increased the potential and thus, the stability relative to the oxidation reaction. Although substituted oligoanilines have not been

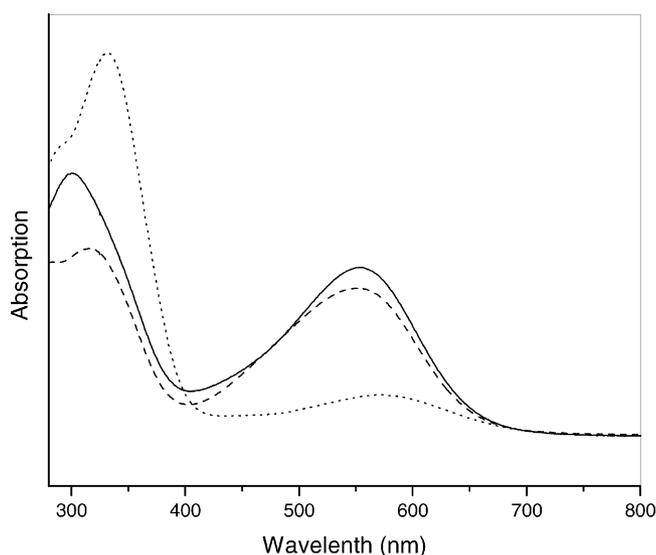


Fig. 3. UV–vis spectra of oxidized trimers in DMF, (1) solid line: APPBD; (2) dash line: APMBD; and (3) dot line: APCBD.

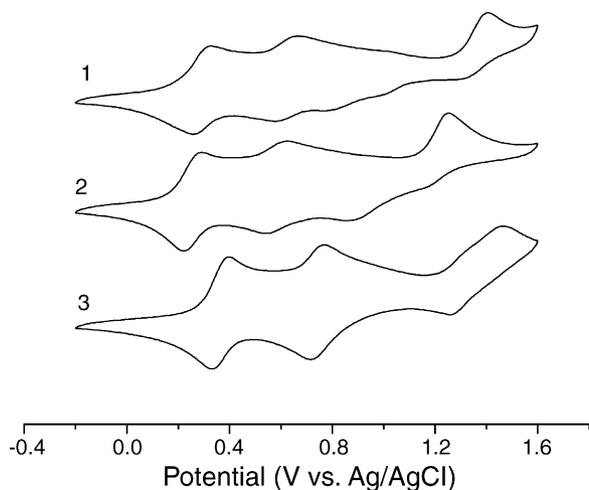


Fig. 4. Cyclic voltammogram of (1) APPBD; (2) APMBD; and (3) APCBD, measured in tetrabutylammonium perchlorate (0.1 M) in acetonitrile with a scan rate of 100 mV/s.

previously studied, a similar trend was observed for the oxidation potentials of aniline derivatives [15,16]. The results were also consistent with the theoretical study by Vaschetto and Retamal [14].

### 3.5. Electrical conductivity

The electrical conductivity of the oligoanilines was measured by a four-point probe method. The oligomers were first doped with iodine vapor for one week, and then pressed into a pellet. The measurement of conductivity was performed at room temperature in a laboratory atmosphere. From Table 1, it is apparent that the electrical conductivity of oligoanilines increased with the chain length of oligomers and conductivity values ranged from  $10^{-6}$  to  $10^{-2}$  S/cm. The conductivity of trimer APPBD was  $6 \times 10^{-3}$  S/cm, consistent with the value reported by Honzl et al. [17]. Trimer APMBD also had a similar conductivity while trimer APCBD was about one order of magnitude lower. As mentioned above, the APCBD had a high oxidation potential and thus, stability to oxidation. The low conductivity of this trimer might be due to the insufficient doping by iodine.

## 4. Conclusion

Substituted trimeric oligoanilines with electron-donating and -withdrawing groups as well as unsubstituted model compounds were synthesized in high yields by palladium-catalyzed aromatic amination. Aniline, 4-methoxyaniline and 4-cyanoaniline reacted with a brominated, functionally pro-

tected aniline dimer using palladium acetate/DPEphos as a catalyst and sodium *tert*-butoxide as a base in toluene at 110 °C, followed by hydrogenolysis and thermolysis. The cyano group remarkably shifted the absorption maximum to longer wavelength in the UV–vis spectra, while the effect of methoxy was negligible. The cyclic voltammetry studies showed that the oxidation potential was affected by the choice of substituent. An electron-donating group (methoxy) lowered the oxidation potential while an electron-withdrawing group (cyano) increased the potential and thus, increased the stability relative to oxidation. The experimental results were consistent with previous theoretical predictions. The conductivity of the iodine-doped oligomers was in the range  $10^{-5}$  to  $10^{-3}$  S/cm.

## Acknowledgements

The authors would like to thank Dr. Peter Zarras, China Lake Naval Air Warfare Center, SERDP program and Rensselaer Polytechnic Institute Start-Up Funds for financial support.

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