

Chemical and Potential-Assisted Assembly of Thiolacetyl-Terminated Oligo(phenylene ethynylene)s on Gold Surfaces

Lintao Cai, Yuxing Yao, Jiping Yang, David W. Price, Jr., and James M. Tour*

Department of Chemistry and Center for Nanoscale Science and Technology, Rice University, 6100 Main Street, Houston, Texas 77005

Received October 22, 2001. Revised Manuscript Received February 13, 2002

Reliable and reproducible methods have been developed for the formation of self-assembled monolayers (SAMs) of thiolacetyl-terminated oligo(phenylene ethynylene)s on a Au surface. The thiolacetyl groups are deprotected in situ and transformed to the free thiol, which then spontaneously forms a SAM. The SAMs are characterized by ellipsometry and electrochemistry, while the solutions are characterized by UV–vis spectroscopy. The results indicate that the previously described $\text{NH}_4\text{OH}/\text{THF}$ mixture is a poor choice for deprotection of thiols bearing multiple nitro substituents. Conversely, use of the more polar system acetone/MeOH/ NH_4OH or acid conditions $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{H}_2\text{SO}_4$ permits the formation of SAMs with thicknesses that are consistent with the predicted length of the molecules. However, the latter acid mixture appears to be less destructive to the highly electron-deficient multinitro oligomers when analyzed by UV–vis spectroscopy. The potential-assisted assembly is 1–2 orders of magnitude faster than the chemical method. This technique can be directly used to assemble different conjugated oligomers on one electrode to the exclusion of a nearby electrode.

Introduction

Self-assembly of organic molecules plays an important role in the construction of ordered nanostructures in molecular electronics.^{1–3} Long-chain alkanethiols and arenethiols^{4,5} have been extensively investigated for chemical and electrochemical assembly^{6–8} on Au surface by Au–S bonding. Hsueh and co-workers⁹ reported the electrochemically directed self-assembly of alkanethiol sulfates on selected Au electrodes for the fabrication of microelectrode sensor arrays. Simple alkanethiols can form dense, well-packed monolayers on Au; however, a serious deficiency is their inability to carry current. Conjugated organic molecules with π -orbital overlap have interesting electronic and optical properties. Rigid-rod conjugated oligo(phenylene ethynylene)s are one family of molecules that have interesting molecular electronic properties. We systematically reported the self-assembly of thiolacetyl-terminated conjugated molecules on Au.^{10,11} Unprotected thiols can form disulfides

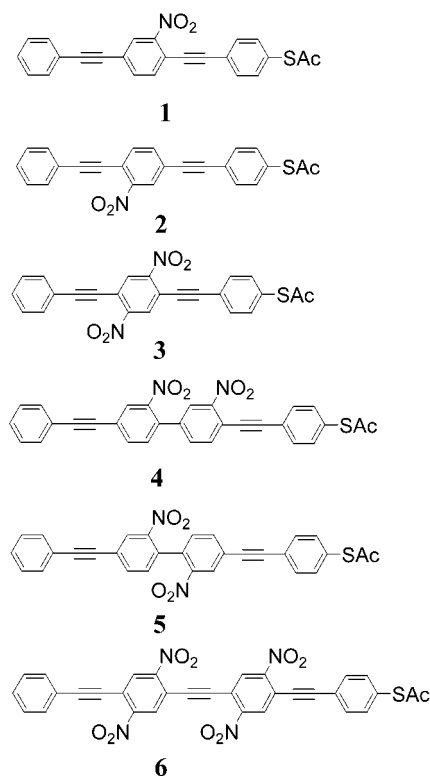
in the presence of a small amount of O_2 , while acetyl-protected thiols provide excellent precursors for generating in situ the oxidatively unstable thiols in order to form SAMs. If substituents are affixed on oligo(phenylene ethynylene)s, a variety of electronic properties, such as negative differential resistance (NDR)^{12–16} and molecular memory devices,¹⁷ can be achieved. Changes in the molecular functionality^{18,19} and conformation^{20,21} are thought to generate changes in the conductivity of the molecular devices, thus producing the molecular-scale switching behavior.

We report here the formation of SAMs via the acid- or base-catalyzed deprotection of thiolacetyl-terminated

- (1) Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791.
- (2) Joachim, C.; Gimzewski, J. K.; Aviram, A. *Nature (London)* **2000**, *408*, 541.
- (3) Reed, M. A.; Tour, J. M. *Sci. Am.* **2000**, *282*, 68.
- (4) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481.
- (5) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533.
- (6) Weisshaar, D. E.; Lamp, B. D.; Porter, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 5860.
- (7) Tender, L. M.; Worley, R. L.; Fan, H.; Lopez, G. P. *Langmuir* **1996**, *12*, 5515.
- (8) Byloos, M.; Al-Maznai, H.; Morin, M. *J. Phys. Chem. B* **1999**, *103*, 6554.
- (9) Hsueh, C. C.; Lee, M. T.; Freund, M. S.; Ferguson, G. S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1228.
- (10) Tour, J. M.; Jones, L.; Pearson, D. L.; Lamba, J. S.; Burgin, T. P.; Whitesides, G. W.; Allara, D. L.; Parikh, A. N.; Atre, S. V. *J. Am. Chem. Soc.* **1995**, *117*, 9529.

- (11) Allara, D. L.; Dunbar, T. D.; Weiss, P. S.; Bumm, L. A.; Cygan, M. T.; Tour, J. M.; Reinherth, W. A.; Yao, Y.; Kozaki, M.; Jones, L.; II *Ann. N.Y. Acad. Sci.* **1998**, *852*, 349.
- (12) Chen, J.; Reed, M. A.; Rawlett, A. M.; Tour, J. M. *Science* **1999**, *286*, 1550.
- (13) Chen, J.; Wang, W.; Reed, M. A.; Rawlett, A. M.; Price, D. W.; Tour, J. M. *Appl. Phys. Lett.* **2000**, *77*, 1224.
- (14) Fan, F. R. F.; Yang, J.; Dirk, S. M.; Price, D. W.; Kosynkin, D.; Tour, J. M.; Bard, A. J. *J. Am. Chem. Soc.* **2001**, *123*, 2454.
- (15) Rawlett, A. M.; Chen, J.; Reed, M. A.; Tour, J. M. *Polym. Mater., Sci. Eng. (Am. Chem. Soc., Div. Polym. Mater.)* **1999**, *81*, 140.
- (16) Seminario, J. M.; Zacarias, A. G.; Tour, J. M. *J. Am. Chem. Soc.* **2000**, *122*, 3015.
- (17) Reed, M. A.; Chen, J.; Rawlett, A. M.; Price, D. W.; Tour, J. M. *Appl. Phys. Lett.* **2001**, *78*, 3735.
- (18) Seminario, J. M.; Zacarias, A. G.; Tour, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 3970.
- (19) Seminario, J. M.; Zacarias, A. G.; Tour, J. M. *J. Phys. Chem. A* **1999**, *103*, 7883.
- (20) Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, L.; II; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705.
- (21) Donhauser, Z. J.; Mantooth, B. A.; Kelly, K. F.; Bumm, L. A.; Monnell, J. D.; Stapleton, J. J.; Price, D. W., Jr.; Rawlett, A. M.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **2001**, *292*, 2303.

Chart 1



oligo(phenylene ethynylene)s containing nitro groups. The SAMs produced with chemical and potential-assisted assembly are characterized by UV-vis spectroscopy, ellipsometry and electrochemistry.

Experimental Section

Gold Substrates. A single-crystal silicon wafer was cut into $6 \times 16 \text{ mm}^2$ sheets and then cleaned for 30 min in a hot (40 °C) fresh acidic peroxide (3:1 $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$, v/v) solution, rinsed with flowing distilled water, ethanol, and acetone, and the pieces of Si were dried in flowing ultrahigh purity N_2 gas. The Au films were deposited by thermal evaporation of 200 nm thick Au onto the Si sheets with a 25 nm Cr adhesion layer at a rate of 1 Å/s under a vacuum of 2×10^{-6} Torr. The Au samples were finally stored in a N_2 atmosphere. Before use, the Au substrates were cleaned by a UV/ O_3 cleaner (Boekel Industries, Inc., model 135500) for 10 min in order to remove organic contamination, followed by ultrasonic cleaning in ethanol for 20 min to remove the resulting Au oxide layer, rinsing with ethanol and acetone, and then drying in flowing N_2 . This procedure was confirmed to provide a clean, reproducible Au surface.^{22,23}

Chemicals. Methylene chloride (CH_2Cl_2) and acetonitrile were distilled from calcium hydride. Tetrahydrofuran was distilled from sodium/benzophenone ketyl. All other chemicals were used as received without further purification. The synthesis of the compounds (Chart 1) have been described elsewhere.^{11,13,24–26}

Base-Promoted Thiol Deprotection. The oligomer (1 mg) was dissolved in a solvent, e.g., ethanol, THF, or mixture of acetone/MeOH (2:1, v/v) in a 4 mL vial to a concentration of about 0.5 mM. Then $10 \mu\text{L}$ of concentrated NH_4OH was added and the mixture was incubated for 10 min in order to deprotect the thiol group. Excess addition of NH_4OH (e.g., $40 \mu\text{L}$) will lead to precipitation. In some case, a $200 \mu\text{L}$ acetone/MeOH solution of 0.3 mM Cs_2CO_3 was also used for the deprotection.

Table 1. Chemical Self-Assembly of Conjugated Thiolacetylated Oligomers in THF

compound	solvent	base	time (h)	thickness (nm)	
				exptl ^a	calcd ^b
1	THF	NH_4OH	24	2.3	2.14
2	THF	NH_4OH	24	2.1	2.14
3	THF	NH_4OH	24	1.0	2.14
4	THF	NH_4OH	24	0.8	2.62
5	THF	NH_4OH	24	0.7	2.62
6	THF	NH_4OH	24	1.6	2.86

^a The value measured by ellipsometry. ^b The theoretical thickness calculated by molecular mechanics without the consideration of the tilt angle of molecule in SAM.

Acid-Promoted Thiol Deprotection. The oligomer (1 mg) was dissolved in a solvent mixture of $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (2:1, v/v) in a 4 mL vial. Then $50\text{--}70 \mu\text{L}$ of concentrated H_2SO_4 was added, and the solution was incubated for 1–4 h in order to deprotect the thiol moiety.

Chemical Assembly. The cleaned Au substrates were immersed into the adsorbate solutions at room temperature for a period of 20–24 h. All the solutions were freshly prepared, previously purged with N_2 for an O_2 -free environment and kept in the dark during immersion to avoid photooxidation. After the assembly, the samples were removed from the solutions, rinsed thoroughly with acetone, MeOH, and CH_2Cl_2 , and finally blown dry with N_2 .

Potential-Assisted Assembly. The electrochemistry experiments were carried out using a BAS CV-50W voltammetric analyzer (Bioanalytical Systems, Inc). A conventional three-electrode cell was used with an Au substrate as the working electrode, a Pt wire as the counter electrode, and an Ag/AgNO_3 (10 mM AgNO_3 and 0.1 M Bu_4NBF_4 in acetonitrile) reference electrode. The monolayers were deposited by applying a constant potential of 400 mV for 5–60 min in the adsorbate solutions. After the deposition, the samples were removed from the solutions, rinsed with acetone, MeOH, and CH_2Cl_2 , and blown dry with N_2 .

Electrochemical Measurement. Cyclic voltammetry (CV) of formed SAMs was performed in an aqueous solution with 1 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 0.1 M KCl between -0.2 and $+0.6 \text{ V}$ (vs SCE) at a rate of 100 mV/s . An Au disk electrode (MF-2014, BAS) with a diameter of 1.6 mm was used as the working electrode, a saturated calomel electrode (SCE) as a reference electrode, and a Pt wire as a counter electrode.

Ellipsometry. Monolayer thickness was determined using a Rudolph series 431A ellipsometer. The He–Ne laser (632.8 nm) light was incident at 70° on the sample. Measurements were carried out before and immediately after monolayer adsorption. All the thicknesses were calculated based on the refractive index of $n_f = 1.55$, $k_f = 0$. The length of the conjugated oligomer was calculated from the sulfur atom to the most distant proton for the minimum energy extended forms by molecular mechanics. The theoretical thickness was then obtained with the assumed linear Au–S–C bond angle and 0.24 nm for the Au–S bond length.

UV–Vis Spectroscopy. The UV–vis spectra were recorded on a UV–vis–NIR scanning spectrophotometer (Shimadzu, UV-3101 PC).

Results and Discussion

As described previously,¹⁰ the thiolacetyl groups of compounds are easily deprotected to the free thiol or thiolate by deacylation with NH_4OH , and then the SAMs are formed on a Au surface by Au–S bonding. Table 1 shows the chemical assembly of conjugated molecules 1–6 in THF solvent. Mononitro compounds 1 and 2 have a similar assembly in ethanol and THF, and their SAM thicknesses are close to the theoretical values. On the other hand, the thicknesses of SAMs of multinitro compounds exhibit a large difference com-

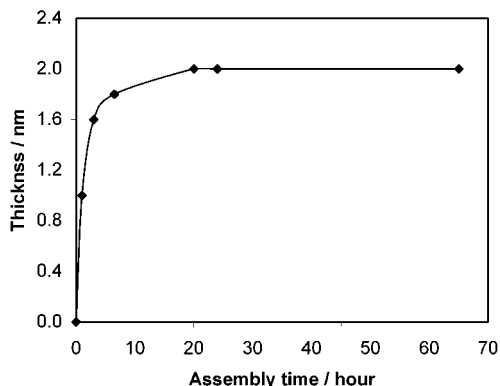
(22) Ron, H.; Matlis, S.; Rubinstein, I. *Langmuir* **1998**, *14*, 1116.

(23) Ron, H.; Rubinstein, I. *J. Am. Chem. Soc.* **1998**, *120*, 13444.

Table 2. Chemical Assembly of Conjugated Thiolacetylated Oligomers in a Solvent Mixture

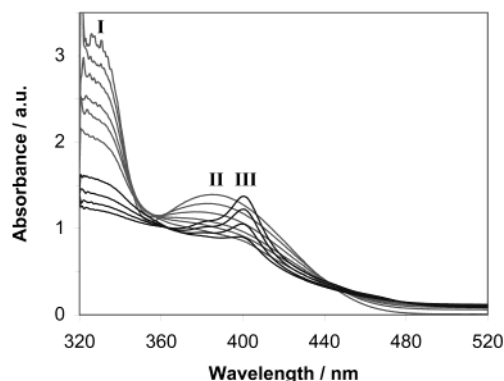
compound	solvent ^a	acid	base	time (h)	thickness (nm)	
					exptl	calcd
3	acetone/MeOH		NH ₄ OH	24	2.0	2.14
4	acetone/MeOH		NH ₄ OH	24	2.5	2.62
5	acetone/MeOH		NH ₄ OH	24	2.4	2.62
6	acetone/MeOH		NH ₄ OH	24	2.0	2.86
3	acetone/MeOH		Cs ₂ CO ₃	24	2.4	2.14
3	CH ₂ Cl ₂ /MeOH	H ₂ SO ₄		24	2.2	2.14
4	CH ₂ Cl ₂ /MeOH	H ₂ SO ₄		24	2.4	2.62
5	CH ₂ Cl ₂ /MeOH	H ₂ SO ₄		24	2.5	2.62
6	CH ₂ Cl ₂ /MeOH	H ₂ SO ₄		24	2.9	2.86

^a The ratio of mixed solvent is 2:1.

**Figure 1.** Growth kinetics of compound **3** chemically assembled on Au in acetone/MeOH/NH₄OH.

pared to the calculated values. A slower rate of adsorption is detected. The strong electron-withdrawing nitro group might lower the Au and S interaction, resulting in the slower assembly rate²⁷ and the poor adsorption on Au surface. Moreover, the multinetro groups of conjugated molecules are possibly attacked in the basic environment during the long assembly time, leading to decomposition of the compounds and inducing precipitation in the solution accompanied by color changes from yellow-green to brown.

To obtain SAMs of multinetro compounds, a mixed solvent was selected based on the solubility and deprotection system. As shown in Table 2, the acetone/methanol solvent mixture performs best in the base-promoted method. The SAMs thicknesses of dinitro compounds **3**, **4**, and **5** are similar to the calculated values after assembly times of 24 h, thus indicating complete assembly. Conversely, the tetranetro compound **6** is not well-assembled; there is a large difference between the measured and calculated thicknesses. Figure 1 shows the growth kinetics of compound **3**. The initial growth is very fast during the first 5 h. The growth rate slows later and reaches saturated coverage after 20 h. A similar phenomenon is observed in the adsorption kinetics^{28–30} of an alkanethiol compound on

**Figure 2.** Time resolution UV-vis spectra of compound **3** in acetone/MeOH/NH₄OH at the different reaction times: peak II, from top to bottom, 0, 5, 10, 15, 20, and 30 min; peak III, from bottom to top, 1, 1.5, 2, and 2.5 h.

Au, in which the main process of film formation is quite fast (1–2 min). The nitro-compounds grow much more slowly in comparison to the assembly of the alkane-thiols. In addition, Cs₂CO₃ is also a good deprotection reagent, but the reaction is more rapid and there may be residual Cs⁺ in SAM films. NH₄OH is easily volatilized and removed by washing and results in a potentially cleaner SAM.

Figure 2 shows time resolution UV-vis spectra of compound **3** in acetone/MeOH/NH₄OH. As the time increases, peak I (330 nm) continuously decreases, and peak II (385 nm) quickly decreases during the first 30 min. After reaction for 1 h, a new peak III appears at 400 nm and continues to increase thereafter. In comparison, the standard reference spectra of free thiol compound **3** shows the two peaks located at 330 and 395 nm. The data indicate that the acetyl-protected thiol is deprotected in about 30 min under basic conditions and decomposition byproducts start to form, displaying the absorbance at 400 nm.

The technique described here using concentrated H₂SO₄ in CH₂Cl₂/MeOH solvent is advantageous. As indicated in Table 2, all the SAMs of compounds **3–6** containing multinetro groups have SAM thicknesses consistent with their calculated values. The data confirms that the acid-promoted method is reliable, especially for the tetranetro compound **6**, which does not effectively assemble by the base-promoted method. H₂SO₄ can catalyze the deacylation reaction and does not appear to attack the nitro groups in the conjugated molecule. Also, the solution is stable and clear without any deposition. The color of the solution remains unchanged after the addition of H₂SO₄.

Figure 3 displays time resolution UV-vis spectra of compound **3** in CH₂Cl₂/MeOH/H₂SO₄. As the time increases, peak I (330 nm) first decreases and red shifts by 8 nm to 338 nm. Peak II (397 nm) first decreases during 1.5 h and then bathochromically shifts by 13 nm to an increased peak III (410 nm) after 4 h. After reaction times of 20 h, the spectrum of the deprotected product is in agreement with the standard spectrum of the free thiol of **3**, as indicated in Figure 4a. The data

(24) Tour, J. M.; Kozaki, M.; Seminario, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 8486.

(25) Tour, J. M.; Rawlett, A. M.; Kozaki, M.; Yao, Y.; Jagessar, R. C.; Dirk, S. M.; Price, D. W.; Reed, M. A.; Zhou, C.-W.; Chen, J.; Wang, W.; Campbell, I. *Chem.-Eur. J.* **2001**, *7*, 5118.

(26) Sonogashira, K.; In *Metal-catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: New York, 1998; pp 203–230.

(27) Liao, S.; Shnidman, Y.; Ulman, A. *J. Am. Chem. Soc.* **2000**, *122*, 3688.

(28) Pan, W.; Durning, C. J.; Turro, N. J. *Langmuir* **1996**, *12*, 4469.

(29) Bain, C. D.; Troughton, E. B.; Tao, Y. Y.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321.

(30) Bensebaa, F.; Voicu, R.; Huron, L.; Ellis, T. H. *Langmuir* **1996**, *13*, 5335.

Table 3. Potential-Assisted Self-Assembly of Conjugated Thiolacetylated Oligomers on Au

compound	solvent ^a	acid	base	potential (mV)	time (min)	reduced ratio of redox peak current ^b (%)
1	EtOH		NH ₄ OH	400	5	99
3	acetone/MeOH		NH ₄ OH	400	60	87
5	acetone/MeOH		NH ₄ OH	400	30	59
5	acetone/MeOH		NH ₄ OH	400	60	95
6	acetone/MeOH		NH ₄ OH	400	60	22
bare Au						0
3	CH ₂ Cl ₂ /MeOH	H ₂ SO ₄		400	60	90
5	CH ₂ Cl ₂ /MeOH	H ₂ SO ₄		400	60	97
6	CH ₂ Cl ₂ /MeOH	H ₂ SO ₄		400	60	96

^a The ratio of mixed solvent is 2:1. ^b The reduced ratio of redox peak current is deduced by $(1 - I_{\text{SAM}}/I_{\text{Au}}) \%$ from CVs in an aqueous solution of K₃[Fe(CN)₆]/KCl.

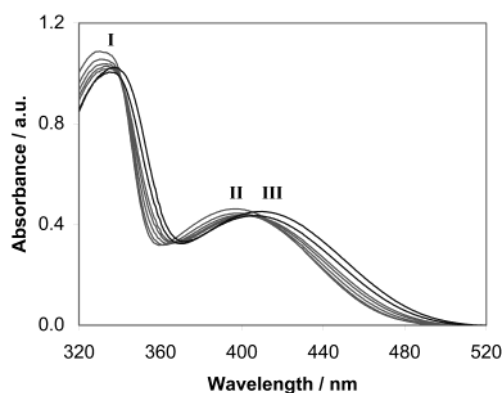


Figure 3. Time resolution UV-vis spectra of compound **3** in CH₂Cl₂/MeOH/H₂SO₄ at the different reaction times: peak II, from top to bottom, 0, 0.5, and 1 h; peak III, from bottom to top, 1.5, 2.5, 4, and 12 h.

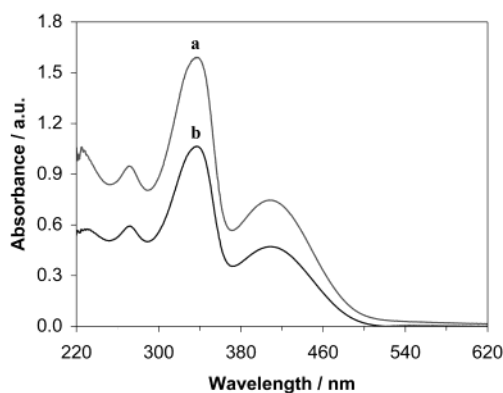


Figure 4. UV-vis spectra: (a) standard reference of free thiol **3**; (b) and deprotected **3** in CH₂Cl₂/MeOH/H₂SO₄ at 20 h reaction time.

indicate that the acid deprotection still maintains the conjugated molecular structure without any decomposition. However, the deprotection time (4 h) in the acid-promoted procedure is slower than that (30 min) in the base-promoted method.

An external electric field applied at the liquid/Au interface can greatly change the assembly reaction rate.^{22–23} Figure 5 illustrates cyclic voltammograms of various SAMs in aqueous solution with 1 mM K₃[Fe(CN)₆] and 0.1 M KCl. For the SAM of compound **5** assembled in acetone/MeOH/NH₄OH solution (Figure 5b) for 30 min, the redox current is decreased by half and the difference between redox peak potentials is increased compared to that of the bare Au electrode (Figure 5a). After 60 min deposition (Figure 5c), the current is greatly decreased and the CV shows a flattened capacitance shape. The electrode is well-

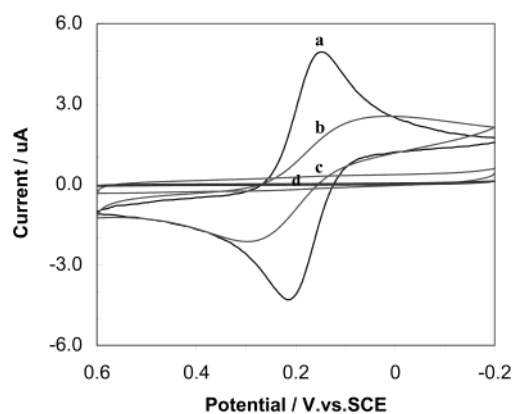


Figure 5. Cyclic voltammograms in the aqueous solution with 1 mM K₃[Fe(CN)₆] and 0.1 M KCl between -0.2 and +0.6 V (vs SCE) at the rate of 100 mV/s: (a) bare Au electrode; (b, c) SAM **5** assembled in acetone/MeOH/NH₄OH for (b) 30 min at 400 mV and (c) 60 min at 400 mV; (d) SAM **1** assembled in EtOH/NH₄OH for 5 min at 400 mV.

blocked by the SAM. In the case of the SAM of compound **1** assembled in EtOH/NH₄OH at 400 mV for 5 min (Figure 5d), the CV shows a flattened line, which means the SAM impedes the mass transport of the large Fe(CN)₆³⁻ ions and results in no electrochemical reaction on Au. The measured thickness of the SAM is 2.2 nm, which is consistent with the calculated value of a monolayer of molecule **1**.

Table 3 summarizes the results of potential-assisted assembly of various molecules on Au electrodes. The assembly rate is fast, and the SAM thickness increases with time. The rate of the potential-assisted assembly is increased 10–100 times compared to the rate of the chemical assembly. In the common chemical assembly, which is a passive incubation process, the open circuit potential (OCP) is about -200 to -300 mV. However, in an external positive electric field, the free thiol and thiolate with negative charge can adsorb strongly on Au; therefore, a modest anodic potential (i.e., 400 mV) can greatly enhance the assembly rate. A lower negative potential will impede the assembly reaction and even peel away the existing SAM.^{31–34} Conversely, a higher positive potential will induce the MeOH and Au oxidation, which also lead to the desorption of the SAM.

(31) Widrig, C. A.; Chinkap, C.; Porter, M. D. *J. Electroanal. Chem.* **1991**, *310*, 335.

(32) Weisshaar, D. E.; Lamp, B. D.; Porter, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 5860.

(33) Gorman, C. B.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1995**, *11*, 2242.

(34) Oyamatsu, D.; Kanemoto, H.; Kuwabata, S.; Yoneyama, H. *J. Electroanal. Chem.* **2001**, *497*, 97.

In the base-promoted electrochemical assembly, the mononitro and dinitro compounds **1**, **3**, and **5** show good assembly and nearly full coverage on Au. The tetranitro compound **6** slowly forms SAMs by base promotion with either the potential-assisted procedure or the chemical method as described in Table 2. By using the acid-promoted electrochemical method, however, all of the nitro compounds **3**, **5**, and **6** can be completely assembled after a 60 min deposition time. The potential-assisted assembly is rapid and reproducible. By careful selection of potential and solution, different conjugated compounds can be deposited on different parts of one electronic device for the construction of a more complex logic circuit in molecular electronics.³⁵

(35) Yang, J.; Tour, J. M. Unpublished data.

(36) Fan, F. R. F.; Yang, J.; Cai, L. T.; Price, D. W.; Dirk, S. M.; Kosynkin, D.; Yao, Y.; Rawlett, A. M.; Tour, J. M.; Bard, A. J. *J. Am. Chem. Soc.* **2002**, *124*, 5550.

Conclusion

We have developed a reliable and repeatable method for formation of SAMs of rigid-rod conjugated oligo-(phenylene ethynylene)s with thiolacetyl end groups. The acid-promotion method has advantages over the base-promoted method for the deprotection of oligomers containing several nitro groups. The systematic electrical measurement^{14,36} of functionalized SAMs to demonstrate the potential application in molecular electronics is ongoing.

Acknowledgment. This work was supported by the Defense Advanced Research Projects Agency (DARPA), the Office of Naval Research (ONR), and the National Science Foundation (NSF-FRG, NSR-DMR-0073046).

CM011509B