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A Method for Removing Self-Assembled Monolayers on Gold

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Self-assembled monolayers (SAMs) have been widely used in studying interfacial phenomena, biological processes, electrochemistry, photoelectrochemistry, photoactivity and molecular interaction. Much research has been carried out in fabricating and removing SAMs on different substrates. In this work, we report for the first time, to our knowledge, that SAMs of thiolates on gold can be removed by immersing SAMs in 0.5 M $NaBH_4$ solution for 10 min. The procedure of removing thiolates was very convenient. Cyclic voltammetry, surface-enhanced Raman spectroscopy, and X-ray photoelectron spectroscopy were used to characterize this process. The results indicated that the SAMs of thiolates on gold can be removed efficiently by $NaBH_4$.

Introduction

Self-assembled monolayers (SAMs) are organic assemblies formed by the adsorption of molecular constituents from solution or gas phase onto the surface of solid or liquid. Many self-assembly systems have been investigated, but monolayers of alkanethiolates on gold are probably the most studied SAMs. There are a number of techniques for characterizing the structure-properties of SAMs.[1–4] SAMs are highly ordered and oriented and can incorporate a wide range of groups. Therefore, SAMs provide a prominent, flexible, and convenient way to generate well-defined organic surfaces with useful and highly alterable chemical functionalities displayed at the exposed interface. In fact, SAMs have been used as model surfaces for studying interfacial phenomena, biological and biochemical processes, electrochemistry, photoelectrochemistry, photoactivity, and molecular interaction.[2–4]

With the development of research, a number of methods have been studied to remove SAMs from different substrates. Polishing or roughening surfaces of metals can remove the SAMs and expose a clean surface on bulk metal substrates. Chemical oxidants such as concentrated acids or piranha solutions ($H_2O_2/H_2SO_4 =$ 1:3) also are effective for cleaning substrates.[5] However, high oxidation of these oxidants can induce strong corrosion of substrates. Especially for the film with a thin adhesive layer of chromium or other active metal, the loss of depositions of films must be considered carefully. Thermal desorption[6] and ion sputtering[7] are convenient techniques for removing SAMs from substrates in ultrahigh vacuum (UHV) environments. But the rigorous conditions limit the use of these two methods. Besides the above methods, two special methods for removing SAMs from metallic substrates have been developed. When a negative potential is applied to the supporting metal, thiolates can be desorbed via reduction.[8–12] A typical desorption potential for *n*-alkanethiolates is -1.0 ± 0.25 V with respect to a Ag/AgCl (saturated KCl) reference electrode.[13] Studies of the mechanism of electrochemical desorption suggest that the desorption occurs first at defect sites.[14] This method is suitable for removing SAMs on electrodes. Another method is photooxidation, in which SAMs of thiolates on gold undergo oxidation upon exposure to ultraviolet (UV) irradiation in air.[15–18] The thiolates convert to sulfonate groups after oxidation. The mechanism for this process has been studied, which indicates that the species responsible for the photooxidation seems to be ozone produced by UV photolysis of O_2.[19,20] Photooxidation can remove thiolates selectively to some extent. It has the advantage of fabricating special patterns by spatial control of SAM composition, although long irradiation time and high power density of UV light (laser or focus of UV irradiation) are needed.

Herein we develop a mild chemical method for removing SAMs of thiolates from gold substrates. This process is very simple, consisting of just immersing the SAM-modified substrates into $NaBH_4$ solution for about 10 min and then rinsing with ethanol and water. Cyclic voltammetry (CV), X-ray photoelectron spectroscopy (XPS), and surface-enhanced Raman spectroscopy (SERS) are used to examine this method. Results suggest that this method is efficient for removing thiolates from gold substrate. In contrast with the methods reported, this method has several merits, including (1) low limit for substrate: bulk, thin film, or electrode substrates are suitable; (2) mild conditions and simple operation: vacuum or special temperature or additional instruments are not necessary; and (3) environmentally friendly: the solvent used herein is H_2O, and EtOH and $NaBH_4$ can decompose

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easily in water. In addition, the gold surface regenerated by this method has good reproducibility for fabricating new SAMs.

Experimental Section

Material and Reagents. 1-Hexadecanethiol (>99%), 1-dodecanethiol (>98%), 1-octanethiol (>98.5%), 1-hexanethiol (>95%), and 4-aminothiophenol (>97%) were purchased from Aldrich. All other chemicals were of analytical grade and used without further purification. Deionized water (18.2 MΩ/cm) was used in experiments.

Apparatus. CV was performed using a CH Instrument (660A, Chenhua Co., Shanghai, China). Gold and platinum disk electrodes ($d = 2$ mm, Chenhua Co., Shanghai, China) served as the working electrodes. Unless otherwise stated, all voltammetry data presented in this paper were acquired at a scan rate of 50 mV/s versus a Ag/AgCl (sat. KCl) reference electrode and a platinum wire auxiliary electrode in 0.1 M KCl as the supporting electrolyte.

Characterization of surface composition has been carried out on a MultiLab2000 X-ray photoelectron spectroscope (V.G. Scientific Ltd. England) using Mg Kα radiation energy (1253.6 eV). An X-ray power of 300 W (15 kV, 20 mA) was used for all analyses. Binding energy of the peak C1s, corresponding to graphitic carbon, was referenced at 284.6 eV.

The SERS testing was conducted with an LABRAM HR800 spectrometer. A 633.8 nm line was used for excitation. A 50× (OLYMPUS LMPlanF1, NA = 0.5) microscope objective was used to excite and collect the Raman signal.

Substrate Preparation. Different types of pretreatment procedures of substrates were performed in experiments. The electrode was polished with 1.0, 0.3, and 0.05 μm of alumina separately, and rinsed thoroughly in deionized water. Then, the electrode was cleaned by CV (20 scans) in the range of 0.0−1.5 V at the scan rate of 100 mV/s in 0.1 M H_2SO_4 solution.

When the gold electrode was used as the substrate for SERS, it needed to be roughened after the cleaning procedure above. The clean gold electrode was electrochemically roughened in 0.1 M KCl solution by 50 oxidation−reduction cycles from −0.4 to +1.2 V at the scan rate 500 mV/s.(Note that an 8 s hold was used on the negative end of the cycles, and a 2 s hold was used at the positive end.) The roughened electrode was then removed from the KCl solution and thoroughly rinsed with deionized water.

The substrates for XPS were gold and platinum slides (99.99%, 5 mm × 5 mm), which were purchased from Shanghai Chemical Reagent Company. These slides were cleaned by sonication in ethanol for 5 min, then immersed in a solution of 3:1:6 $HCl/HNO_3/H_2O$ for 10 min, and finally rinsed with deionized water.

Monolayer Preparation. The general procedure for monolayer preparation was to expose a gold or platinum substrate to a solution of thiol. The concentration of thiol was 1 mM in ethanol and the total time elapsed during a monolayer preparation was 24 h.

Removing the Monolayer. The substrate modified by the SAM was immersed in 0.5 M $NaBH_4$ solution in 1:1 H_2O/EtOH for 10 min, and then rinsed with ethanol and water.

Results and Discussion

Cyclic voltammetry. CV is sensitive to examine the nature and extent of structural defects of SAMs. Two measurable parameters obtained from CV were usually used to indicate the structure of SAMs. The integrated area of redox peaks indicated the transferred charge, which related to the coverage of electrode. Another indication was charge current, which implied the defects in the monolayer. The defects in SAMs were significant in determining the current response in experiments where the SAM acted as a blocking layer.[21,22] If the size of defects in SAMs was large enough, electroactive species could access the electrode surface through these defects (pinholes). The area fraction of pinholes in SAMs could be estimated by the currents and integrated areas of redox peaks.[22] $Fe(CN)_6^{3-}$ was selected as the electrochemical probe since it represented a convenient and electrochemically reversible, one-electron, outer-sphere redox couple. Figure 1 presents the cyclic voltammogram of $Fe(CN)_6^{3-}$ on different Au electrodes. Figure 1a is the cyclic voltammogram of a bare gold electrode in 1 mM Fe(CN) $_6^{3-}$ solution. The response of the electrode modified by the 1-hexadecanethiol SAM in 1 mM $Fe(CN)_6^{3-}$ is shown in panel b of Figure 1. When the SAM of 1-hexadecanethiol on a gold electrode was removed by $NaBH_4$, the cyclic voltammogram was presented as panel c in Figure 1. There was a dramatic difference between the $i-E$ responses for $Fe(CN)_6^{3-}$ at the monolayer-covered and bare gold electrodes. The reduction current of $Fe(CN)_6^{3-}$ was less by a factor of $>10^2$ at the SAM-modified electrode than that at bare electrode. The low current of the monolayer-covered electrode implied that solution ions could not easily penetrate the organic film and the SAM of $C_{16}H_{33}SH$ on the gold electrode was well-organized.[21,22] In contrast, the $i-E$ responses of $Fe(CN)_6^{3-}$ at the electrode that was treated by 0.5 M $NaBH_4$ in 1:1 H_2O/EtOH was similar to the response at the bare electrode, and the recovery of the current and integrated area of the redox peaks was >95%. The results above indicated that $NaBH_4$ was efficient to remove the SAM of $C_{16}H_{33}SH$ on gold.

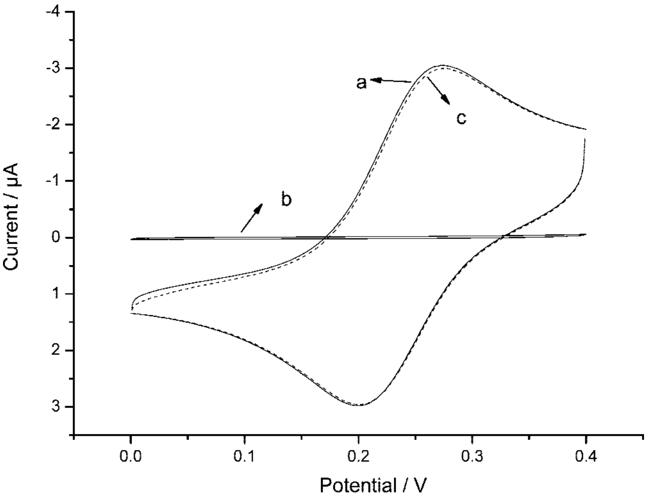

Figure 1. Cyclic voltammogram at different electrodes: (a) bare; (b) $C_{16}H_{33}SH$ monolayer-covered; and (c) removing $C_{16}H_{33}SH$ monolayer with $NaBH_4$. Scan rate: 50 mV/s; solution condition: 1 mM $Fe(CN)_6^{3-}$ in 0.1 M KCl.

With the increase of immersion time for SAMs-modified electrode in 0.5 M $NaBH_4$, the change of currents on different SAMs-modified electrodes were shown in Figure 2. When the immersion time was longer than 10 min, all SAMs therein could be removed completely. The chain length of *n*-alkanethiolates also affected the removal of SAMs on gold. When the chain length decreased, the immersion time for completely removing SAMs became shorter. An interpretation for this change was that the diffusion of $NaBH_4$ to the substrate was different. The rigidness of SAMs and the molecular interaction (van der Waals and hydrophobic interaction) between molecules in SAMs decreased when the chain of *n*-alkanethiolates became short.[1−4] Meanwhile, the defect sites in SAMs of short-chain *n*-alkanethiolates increased.[1,3,4] This could be confirmed by the increasing of charge currents (the currents in Figure 2, $t = 0$) on fresh SAMs-modified electrodes. Therefore, it was relatively easier to remove the SAMs of short-chain *n*-alkanethiolates because $NaBH_4$ had more chance to approach the substrate by diffusion.

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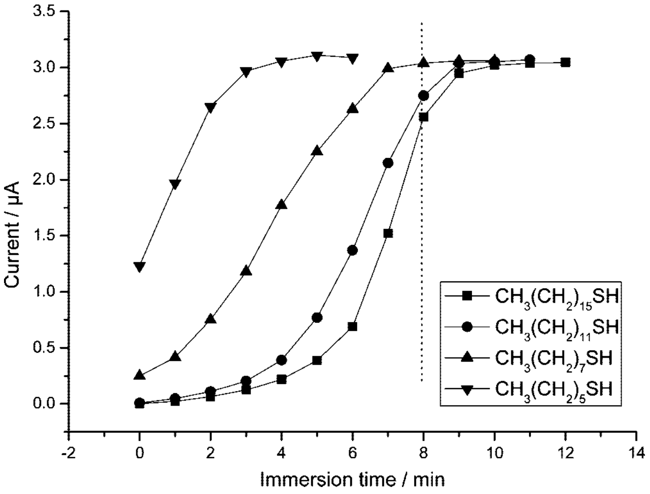

Figure 2. Current at 0.27 V after immersing SAMs-modified electrodes in 0.5 M $NaBH_4$ for different times. Scan rate: 50 mV/s; solution condition: 1 mM $Fe(CN)_6^{3-}$ in 0.1 M KCl.

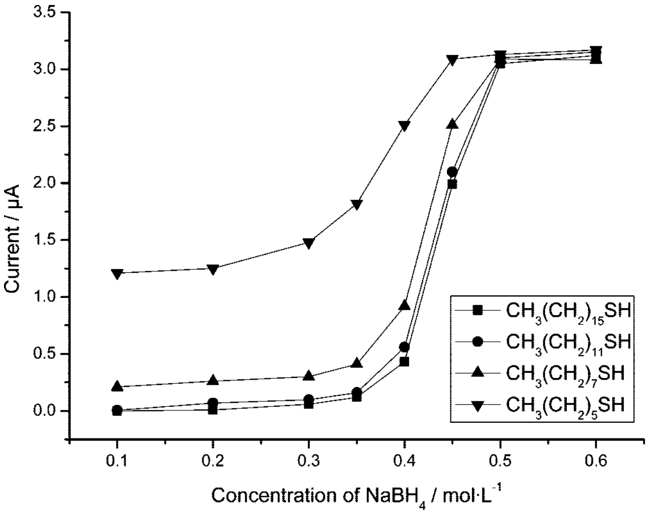

Figure 3. Current at 0.27 V after immersing SAMs-modified electrodes in different concentrations of $NaBH_4$ for 10 min. Scan rate: 50 mV/s; solution condition: 1 mM $Fe(CN)_6^{3-}$ in 0.1 M KCl.

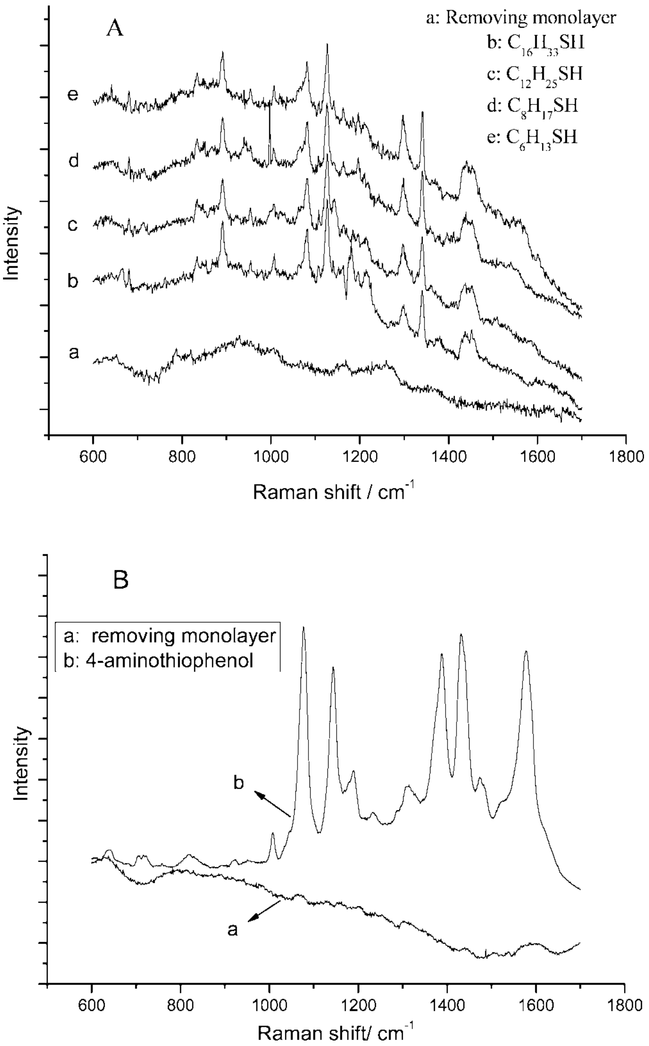

Figure 4. (A) SER spectra of different gold surfaces: treated by $NaBH_4$ (a); modified by SAMs of $C_{16}H_{33}SH$ (b), $C_{12}H_{25}SH$ (c), $C_8H_{17}SH$ (d), and $C_6H_{13}SH$ (e). (B) SER spectra of different gold surfaces: treated by $NaBH_4$ (a); modified by SAMs of 4-aminothiophenol (b).

When the immersion time increased, the increase of the current in Figure 2 was not equal. It was accelerated at the first stage and then slowed down. This change indicated that the increase of electrode-active surface area had a trend that was the same as the current increase, and the desorption of SAMs occurred first at defect sites. At the first stage, the desorption of molecules around defects increased the edge area of defects, which can improve the contact between $NaBH_4$ and substrate modified by SAMs. Then the removal rate of SAMs and the increasing of active surface area were accelerated. The increase of current became faster and faster in this stage. After removing most of the SAMs, the increase of active surface area became slow and the current increase slowed down.

$NaBH_4$ solutions with different concentrations were used to remove the SAMs on gold electrodes. The results are shown in Figure 3. The increase of $NaBH_4$ concentration can speed the desorption of SAMs. High concentration of $NaBH_4$ increased the concentration difference between bulk solution and substrate surface, which can improve the diffusion of $NaBH_4$ itself. When the chain length of *n*-alkanethiolate increased, the penetration of $NaBH_4$ became hard. Higher concentration of $NaBH_4$ was needed to remove the SAMs. In this work, 0.5 M was used to remove the SAMs of *n*-alkanethiolates with carbon chain lengths less than 16.

SAMs-modified Pt electrodes were also investigated by CV (Supporting Information). They showed properties very similar to those of Au electrodes. 0.5 M $NaBH_4$ solution and 10 min were suitable for removing SAMs of *n*-alkanethiolates with carbon chain lengths less than 16 from Pt substrates.

Surface-Enhanced Raman Spectroscopy. SERS is an efficient technique for molecules on surfaces because of high sensitivity and finger printing. Monolayers formed from 4-aminothiophenol and *n*-alkanethiols ($C_6H_{13}SH$, $C_8H_{17}SH$, $C_{12}H_{25}SH$, and $C_{16}H_{33}SH$) were characterized by SERS. Figure 4A,B shows the spectra of SAMs formed from *n*-alkanethiolates and 4-aminothiophenol on gold separately. The peaks in Figure 4A at 678 (C−S), 908 (C−C), 1080 (C−S), 1126 (C−C), 1290 (CH_3), 1345 (CH_2), 1458 (CH_3) cm^{-1} were responses to $CH_3(CH_2)_{n-1}S{-}Au$. In Figure 4B, the response of SAM was strong because of the existence of phenyl, and the peaks were easily assigned: 1007 (C−C), 1078 (C−S), 1150 (C−C), 1410 (C−N), 1459 (CH), 1582 (CH) cm^{-1}. After removing the monolayers from gold substrates with $NaBH_4$, the responses of SAMs disappeared, as shown in Figure 4A,B. The results indicated that the molecules adsorbed on gold with a chemical bond were removed by $NaBH_4$.

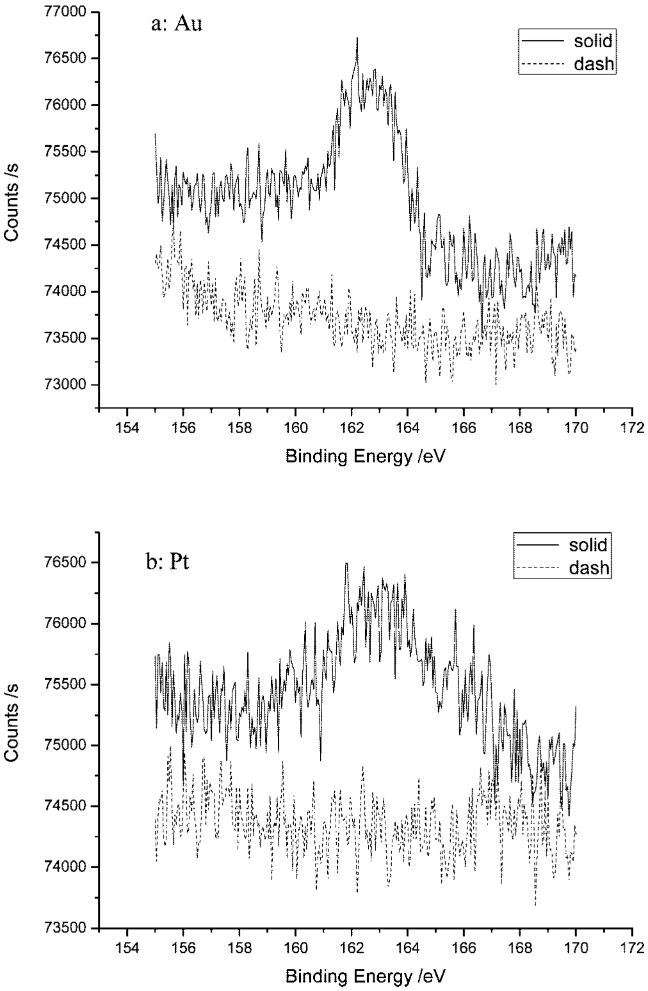

Figure 5. a. S 2p XPS spectra for a monolayer of $C_{16}H_{33}SH$ on Au (solid line) and removing the $C_{16}H_{33}SH$ monolayer with $NaBH_4$ from Au (dashed line). (b) S 2p XPS spectra for a monolayer of $C_{16}H_{33}SH$ on Pt (solid line) and removing the $C_{16}H_{33}SH$ monolayer with $NaBH_4$ from Pt (dashed line).

X-ray Photoelectron Spectroscopy. Figure 5 shows the S 2p region of the X-ray photoelectron spectrum for SAMs ($C_{16}S{-}Au$ and $C_{16}S{-}Pt$) and samples treated by $NaBH_4$ solution. The position of the S 2p of the SAM (solid line in Figure 5 a,b) within the range of 162−165 eV were expected for thiolates (RS−Au and RS−Pt), corresponding well with the reported values for SAMs of alkanethiol on Au or Pt.[17,23,24] In contrast, the S 2p peaks were not detected after removing SAMs with $NaBH_4$ (dashed line in Figure 5 a,b). One reasonable explanation for this change was that the bond cleavage of S−Au and S−Pt induced the loss of S. This conclusion was consistent with the results of CV and SERS. We proposed the following equation for the desorption of SAMs from Au or Pt substrate in the presence of $NaBH_4$:

$$R{-}S{-}M \xrightarrow{NaBH_4} R{-}S{-}H + M^0 \qquad (1)$$

When thiols were desorbed from substrates, they diffused away from the surface into solvent. Because the concentrations of thiols were very low, it was difficult to reconstruct new SAMs on these substrates.[1,2] In fact, the results of XPS indicated that S−M was not able to be detected after removing SAMs with $NaBH_4$.

Reproducibility of Substrate. After removing SAMs by $NaBH_4$, the Au and Pt substrates were used directly to fabricate new SAMs. Electrochemical examinations indicated that the new SAMs were well-organized. When a substrate was used repeatedly to fabricate SAMs more than four times, the charge current at the SAMs-modified electrode would increase, although the redox peaks of $Fe(CN)_6^{3-}$ were not observed. The results suggested that this method can be used to regenerate Au and Pt substrates with good reproducibility.

Conclusion

The results of CV, SERS, and XPS verify that well-organized monolayers of thiolates on gold can be removed efficiently by 0.5 M $NaBH_4$ in 1:1 H_2O/EtOH. The removing of long-chain *n*-alkanethiolate needs longer immersion time and a higher concentration of $NaBH_4$. The thiolates are desorbed via the cleavage of S−Au, and this desorption process occurs first at defect sites. Gold substrates can be regenerated to fabricate new monolayers by this method without further treatment procedures. This method has good applicability for removing SAMs of thiolates on gold because of its mild conditions and simple operation.

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Supporting Information Available: Detailed cyclic voltammetry at SAMs-modified Pt electrodes; scanning tunneling microscopy testing on gold film. This material is free of charge via the Internet at http://pubs.acs.org.

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