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Hygroscopic Effects on AuCl₃-Doped Carbon Nanotubes

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Hygroscopic effects on AuCl₃-doped single-walled carbon nanotubes (SWCNTs) were investigated. Various concentrations of AuCl₃ solution were dropped on the random network SWCNT transistors, where the doping effect was confirmed by $I-V_g$ characteristics and a blue shift in the Raman G band. The AuCl₃-doped SWCNT transistor was highly sensitive to water vapor in the $I-V_g$ curve, especially in the positive gate bias region, compared with the undoped SWCNT transistors. We also found the selective response of water from ambient gases, such as O₂ and N₂, in AuCl₃-doped SWCNTs. This investigation could be beneficial for high-performance water sensor applications.

1. Introduction

Single-walled carbon nanotubes (SWCNTs) have been attracting attention for use in high-performance transistors due to their high mobility and high current carrying capability.^{1–7} Pristine SWCNT transistors exhibit p-type behavior in air and ambipolar behavior in vacuum.⁸ Ambipolarity in SWCNTs has been seen as a drawback compared with Si technology, which prefers the use of unipolar transistors, although ambipolar transistors could be advantageous in some cases for improving integration density.⁹ Extensive studies have been conducted on methods for obtaining n-type and p-type transistors.^{8–22} Because all of the carbon atoms are exposed to the surface in such transistors, the carrier type can be easily modified by the type of adsorbates that are used. The underlying mechanism of determining the carrier type involves choosing an appropriate chemical adsorbate with reduction potentials that are different from those of the carbon nanotube.²³ For instance, n-type dopants, such as polyethylenimine (PEI), viologen, and nicotinamide adenine dinucleotide (NADH), can donate electrons to nanotubes due to their larger negative values compared with nanotubes.^{8,12,14,17,18,20} Conversely, p-type dopants, such as tetrafluorotetracyano-*p*-quinodimethane (F₄TCNQ) and AuCl₃, can extract electrons from nanotubes due to their larger positive values compared with nanotubes.^{10–16,21}

Despite the tremendous effort that has been taken in identifying appropriate dopants, control of doping levels and the environmental effects on the doped nanotubes have been rarely investigated. The stability of n-type dopants has been of particular interest due to the dedoping effect that occurs upon exposure to air.¹⁷ The effect of air instability could be less severe for p-type dopants than for n-type dopants. Furthermore, other phenomena apart from carrier mobility and conductivity and air stability modulation, which can happen through doping with

organic or inorganic materials, have not been paid much attention in the literature and are currently not well-evaluated.

In this report, AuCl₃ doping of a nanotube transistor was robustly controlled by simply dropping a solution of AuCl₃ onto the device. The on/off ratio, mobility, and G- and G'-band shifts demonstrated consistent control of doping. We found that doped nanotube transistors exhibited more severe hygroscopic effects than undoped nanotube transistors. In particular, O₂ adsorption on AuCl₃-doped SWCNT transistors produced a negligible change in current. The selective adsorption of H₂O gas on AuCl₃-doped SWCNTs could be advantageous for designing water sensors with no affinity for O₂ gas.

2. Experimental Methods

Random network SWCNTs were fabricated by remote water-plasma enhanced chemical vapor deposition (PECVD) as previously reported.²⁴ Ferrocene (0.01 M) was mixed with a photoresist and spin-coated on selectively designed channel regions of SiO₂ (thickness = 400 nm), followed by the burning of the photoresist at 600 °C for 30 min. Random network SWCNTs were synthesized at 450 °C with methane gas (60 sccm) and a radio frequency power of 15 W. Ti (10 nm)/Au (100 nm) were deposited as source and drain materials to integrate an array of 200 transistors (channel length = 10 μm, width = 40 μm). A schematic is provided in Figure 1. Gold chloride (AuCl₃) powder was purchased from Sigma-Aldrich. Different concentrations of AuCl₃ were dissolved in nitro-methane, followed by sonication for 5 min. AuCl₃ solutions (30 μL) were dropped on the transistor by a micropipet and spin-coated at 3000 rpm for 30 s after a 30 s residual time.

$I-V_g$ characteristics were measured with a parameter analyzer (Agilent 4156C) using a probe station under ambient conditions. For the gas test, the chamber was maintained at a vacuum of 10⁻¹ Torr and gases (N₂, O₂, and H₂O) were introduced. To compare before and after doping, the channel region of the CNT transistor was taken by field emission scanning electron microscopy (FESEM, JSM7000F, JEOL) with a 1 kV acceleration voltage. Raman spectroscopy (Ranishaw RM1000-Invia) with an excitation wavelength of 633 nm was performed to assess the doping effect based on the G-band shift.

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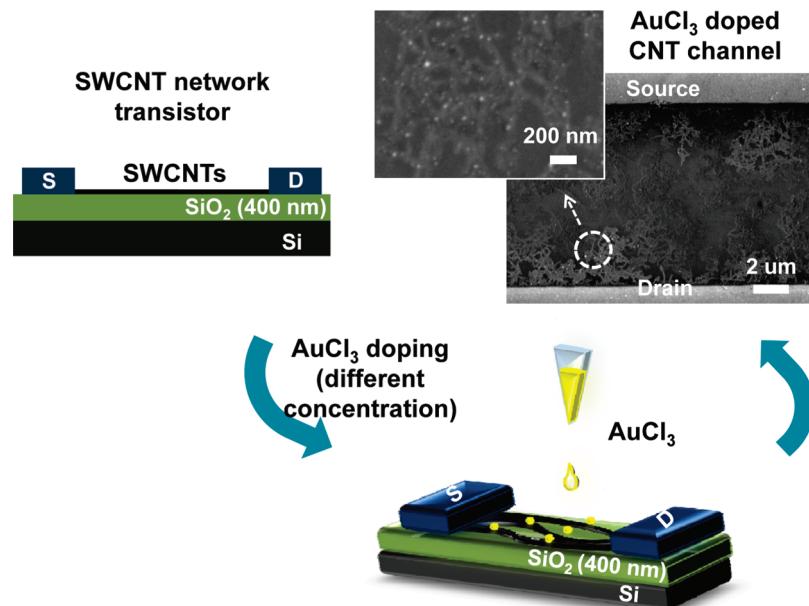


Figure 1. Schematic of a SWCNT network transistor and AuCl₃ doping. The SEM images of the AuCl₃-doped SWCNT channel region.

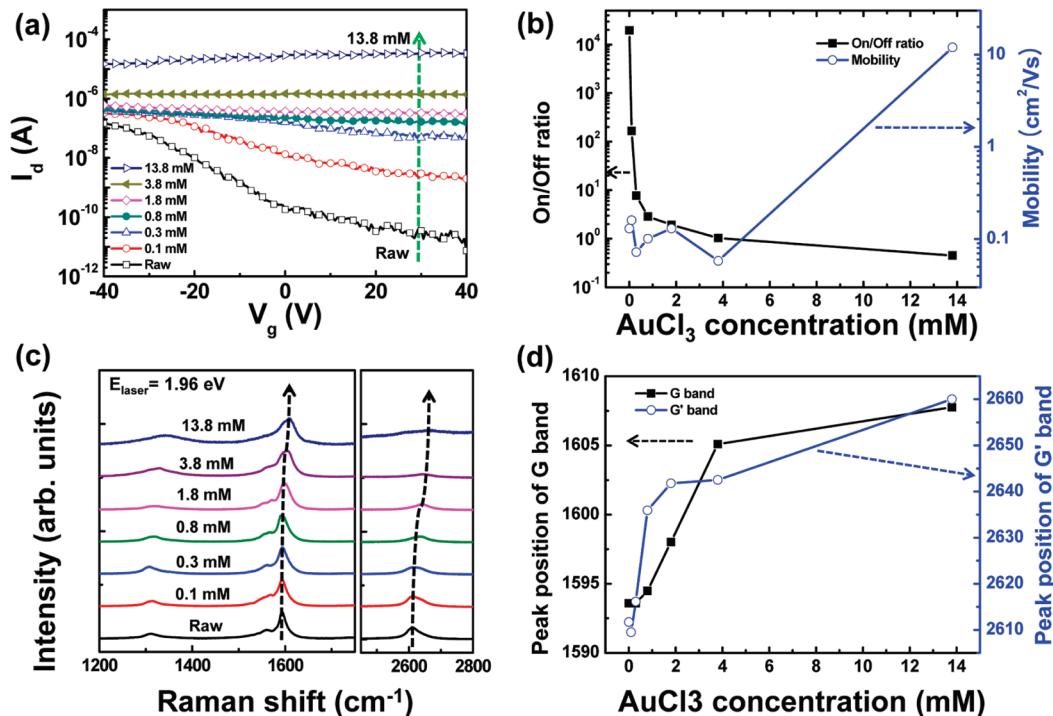


Figure 2. (a) I – V_g characteristics of a random network SWCNT transistor, (b) extracted on/off ratio and mobility, (c) Raman spectra, and (d) peak position of G and G' bands as a function of AuCl₃-doping concentration.

3. Results and Discussion

AuCl₃ was dissolved into Au³⁺ and 3Cl⁻ in nitromethane. We expected that the Au³⁺ ions, which have a high reduction potential compared with that of SWCNTs, would extract electrons from the SWCNTs. As shown in Figure 1, Au³⁺ was reduced and deposited on the nanotube walls and substrates, leaving Au particles on the SWCNTs' surface and also on the substrate. To observe the doping effects of AuCl₃ on the CNT transistor, I – V_g characteristics and Raman spectroscopy were measured by increasing the AuCl₃ concentrations in a single device, as shown in Figure 2. As the doping concentration increased, the hole current level increased gradually, while the off current increased rapidly.^{10,11,15,21} As summarized in Figure

2b, the on/off ratio decreased very rapidly within the low doping concentration region and was saturated at high doping concentrations. Perhaps what is more appropriate to demonstrate the doping effect in I – V_g curves is a threshold voltage (V_{th}) (linear I – V curve instead of log(I)– V curve; see the Supporting Information, Figure S1). V_{th} , a crossover voltage that the slope meets at zero current – $1/2V_{SD}$, was simply shifted to the right side as the doping concentration increased.²⁵ This is clear evidence of a p-doping effect. A similar effect has also been observed.^{10,11,15,21}

The mobility μ_m was calculated by the formula, $\mu_m = (L/V_d)C(W)(dI/dV_g)$, where L is the channel length (10 μm), V_d is the source/drain voltage ($V_d = 2$ V), C is the insulator

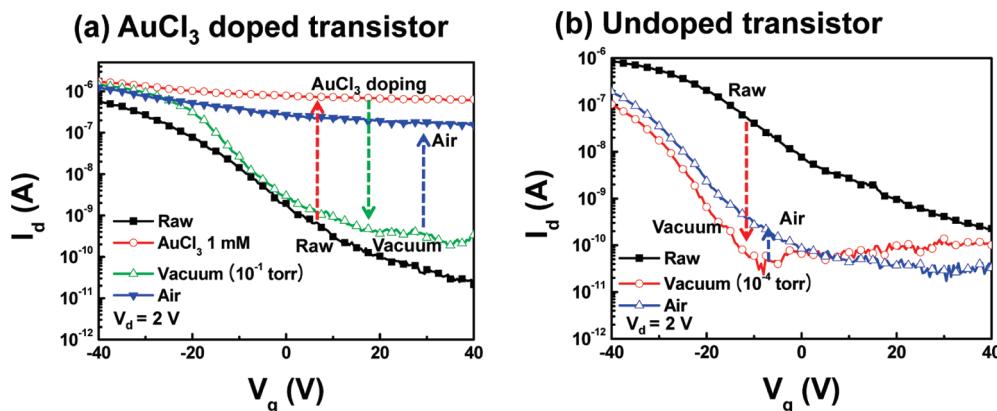


Figure 3. $I-V_g$ characteristics of the (a) AuCl_3 -doped SWCNT transistor and (b) undoped SWCNT transistor under various environments. $I-V_g$ measurements were repeated for the pristine sample, AuCl_3 -doped, AuCl_3 -doped at vacuum, and again exposed to air.

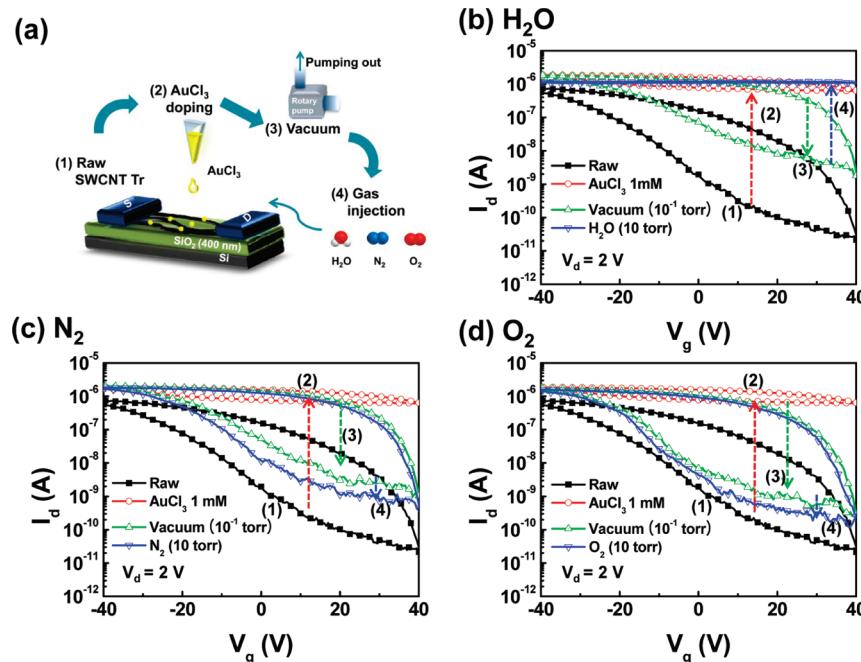


Figure 4. Schematic of the experimental procedure in sequence (a) and the corresponding $I-V_g$ characteristics of the AuCl_3 -doped CNTFET with different gases, (b) H_2O , (c) N_2 , and (d) O_2 . Each number in (a) corresponds to the procedure in (b-d).

capacitance per unit area for 400 nm of SiO_2 , and W is the channel width ($40 \mu\text{m}$).²⁶ The linear slope region was taken for mobility calculations. The mobility did not increase rapidly at low doping concentrations, which was in good contrast with the rapid decrease of the on/off ratio. At high doping concentrations, the mobility increased rapidly, as shown in Figure 2b. The transconductance increased significantly in this case due to high current. The doping effect was well observed through the on/off ratio over a wide range of doping concentrations, whereas the mobility of the transistor did not change appreciably, particularly at low doping concentrations. The correlation between these two properties remains unclear. The peak positions of the G and G' bands in Raman spectra indicated that a blue shift occurred with increasing doping concentrations, supporting the p-doping of nanotubes. Both the G and the G' bands exhibited rapid changes in the low doping concentration region. We noted that the changes in the on/off ratio and mobility were more sensitive than the G- and G'-band shift, indicating that the doping effect can be more vividly observed in the transistor than in the SWCNT solution.

To assess the stability of the device, a transistor doped with 1 mM AuCl_3 was placed into the analyzer chamber and

subjected to a vacuum of 10^{-1} Torr. To our surprise, the off current was significantly suppressed, whereas the on current did not change significantly under vacuum, as shown in Figure 3a. When the transistor was re-exposed to air, the off current recovered to a level similar to that of the original air-exposed transistor. This phenomenon was repeated for several cycles in a similar manner. Comparative measurements were also performed for an undoped sample (Figure 3b). After maintaining the vacuum up to 10^{-4} Torr, both on and off currents were reduced, indicating simple desorption of the adsorbates that originally gave rise to p-doping. Indeed, the current was slightly recovered, but not to the extent of the pristine sample, indicating that the AuCl_3 -doped SWCNTs were more air-sensitive.

To understand this phenomenon in detail, different gases, such as nitrogen, oxygen and water vapor, which are the main components in air, were introduced into the vacuum chamber. A schematic of this experimental procedure is given in Figure 4a. Hysteresis of $I-V_g$ curves was observed in the doped and undoped transistors.³⁰ The pristine sample exhibited an on/off ratio of $\sim 10^4$. With AuCl_3 -doping, both on and off currents were increased by a factor of 3. When the vacuum was maintained at 10^{-1} Torr, the off current was decreased to 10^{-9} A , increasing

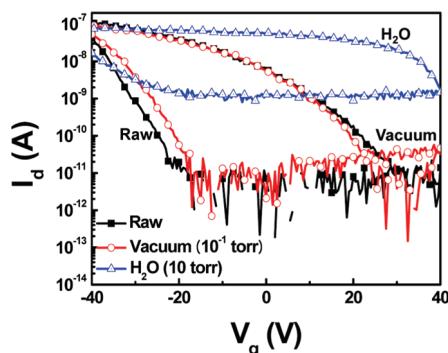


Figure 5. $I-V_g$ characteristics of the undoped SWCNT transistor under H_2O environments.

the on/off ratio to 10^3 . After exposing the transistor to H_2O , the on current was slightly decreased compared with the vacuum level, whereas the off current recovered to a level similar to that of the $AuCl_3$ -doped transistor in air (Figure 4b). The increased off current due to water adsorption was also observed in double-walled CNT transistors.²⁷

Similar experiments were performed for N_2 and O_2 , respectively, as shown in Figure 4c,d. Once the vacuum was maintained, these gases were introduced into the chamber. Unlike the case of H_2O , no noticeable change in current was observed, although the off current level was slightly decreased because of a longer evacuation time. In particular, when O_2 gas was introduced after maintaining the vacuum, the current level decreased slightly over the wide range of the gate voltage. The effect of O_2 gas may be negligible in this case because the change in the current by O_2 gas was small. In addition, the selective hygroscopic effect and the negligible changes of the $I-V_g$ curve with O_2 in the doped SWCNT transistor were somewhat unexpected phenomena compared with those of the pristine SWCNT transistors.

We identified a hygroscopic effect in the $AuCl_3$ -doped SWCNT transistor, which was different from that observed in an undoped SWCNT transistor, as shown in Figure 5. $I-V_g$ characteristics of the undoped SWCNTs were measured similarly as described above. H_2O was introduced to a chamber that had been vacuumed to 10^{-1} Torr. Following introduction of H_2O , the off current increased from $\sim 10^{-11}$ to 10^{-9} A, whereas the on current decreased slightly. The current level recovered to that of the pristine transistor when water vapor introduction was stopped and the vacuum was maintained again. This phenomenon was similar to the $AuCl_3$ -doped SWCNT transistor, with the difference being that the change of the pristine transistor was much less significant. Together, these data confirmed that the $AuCl_3$ -doped SWCNT transistors were much more sensitive to water.

The interpretation of the water adsorption effect on the electrical properties of SWCNT transistors has remained controversial for over a decade. Several studies claimed that electrons are transferred from adsorbed water molecules to nanotubes;²⁸ however, it was later found by more careful theoretical studies that a water molecule has a much larger highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap that does not match with those of SWCNTs, and thus, the charge transfer between the two is negligible.²⁹ Water molecules have also been suggested as the origin of hysteresis due to the substrate adsorption.³⁰ Recently, the charge transfer through the O_2/H_2O couple redox reaction suppresses electron conduction in field effect transistors.³¹ Yet, the role of the water molecule without O_2 has not been clarified. In our case, the difference of O_2 and H_2O was clearly shown, but it was difficult to conclude that the increased off current by water adsorption originates from larger hysteresis or other reasons. We propose a possible mechanism for the explanation of our work in Figure 6. Initially, Au^{3+} ions attract electrons from the nanotube by the reduction potential difference when

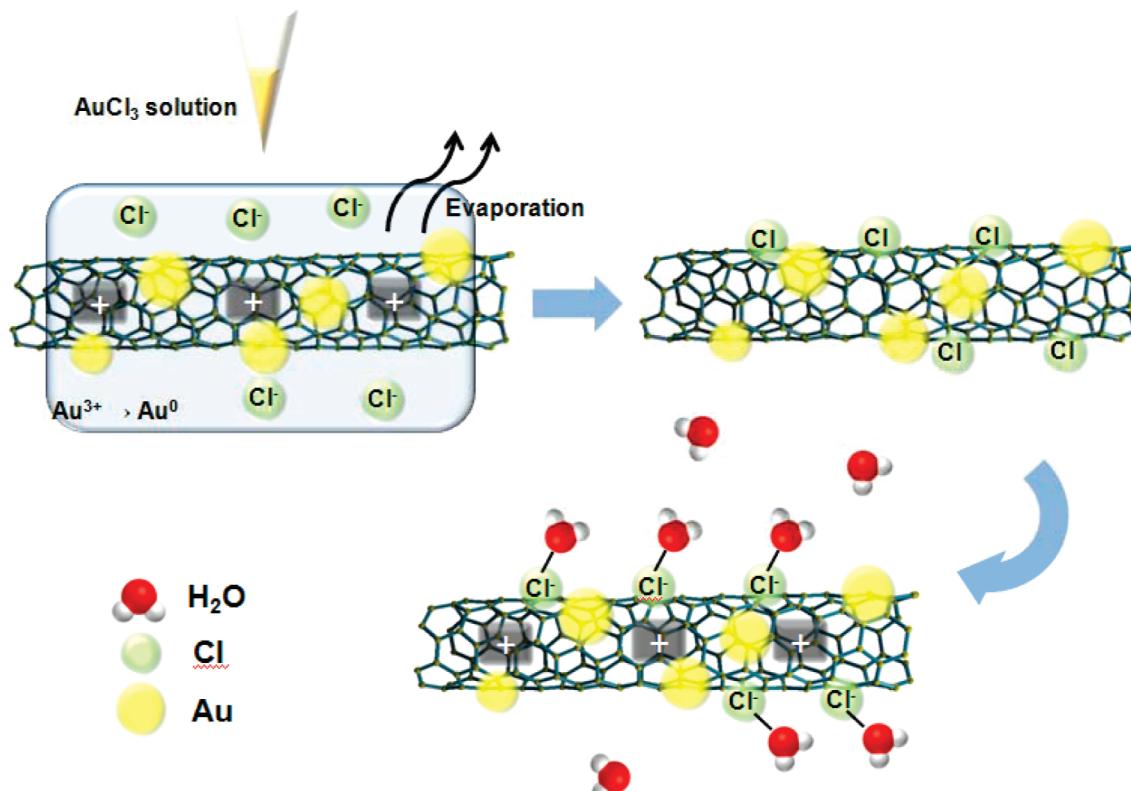


Figure 6. Proposed mechanism of p-doping by $AuCl_3$ and the effect of water adsorption.

AuCl_3 solution is dropped onto CNTs. The Au ion is reduced to Au^0 , and instead, the nanotube is positively charged and stable in solution. After solution evaporation, a Cl^- ion is attached to the nanotube for charge neutrality. The CNT–Cl structure shows p-type behavior. H_2O molecules can easily attach to the Cl atom to enhance the binding energy. Furthermore, p-doping is enhanced as well.³² In fact, our X-ray photoemission spectroscopy analysis confirms that Au^{3+} ions were reduced by electron transfer from SWCNTs, but a significant amount of gold still remained as AuCl_3 salt (see the Supporting Information, Figure S2). Thus, the hygroscopic nature of AuCl_3 salt may be associated with enhanced water adsorption around Cl atoms or Au–Cl clusters on SWCNTs, as predicted from theory.³² At first glance, the environmentally sensitive properties of AuCl_3 -doped SWCNT transistors may be considered as a drawback for electronic applications. However, due to their selectively sensitive characteristics, such transistors may prove useful for developing high-performance water sensors.

4. Conclusions

Different concentrations of AuCl_3 solutions as a strong p-type dopant were chosen to control the doping levels of SWCNT transistors. This dopant was strongly dependent on ambient environmental effects. The on current maintained a p-doping state, whereas the off current changed significantly depending on the presence of air. By separately investigating the $I-V_g$ characteristics of several gases, namely, H_2O , O_2 , and N_2 , we concluded that the AuCl_3 -doped SWCNT transistor exhibited a clear selective water adsorption on the SWCNT transistor compared with O_2 and N_2 gases. We believe that the enhanced hygroscopic effect on AuCl_3 -doped SWCNTs can be utilized for developing selective gas sensors for O_2 in the near future.

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Supporting Information Available: Linear $I-V_g$ curves with different doping concentrations (Figure S1) and X-ray photoemission spectroscopy (XPS) analysis on AuCl_3 -doped SWCNTs (Figure S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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