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Dissymmetric Carbon Nanotubes by Bipolar Electrochemistry

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ABSTRACT

Short carbon nanotubes have been modified selectively on one end with metal using a bulk technique based on bipolar electrochemistry. A stabilized suspension of nanotubes is introduced in a capillary containing an aqueous metal salt solution, and a high electric field is applied to orientate and polarize the individual tubes. During their transport through the capillary under sufficient polarization (30 kV), each nanotube is the site of water oxidation on one end and the site of metal ion reduction on the other end with the size of the formed metal cluster being proportional to the potential drop along the nanotube.

To extend the potential application spectrum of carbon nanotubes (CNTs), it is essential to modify their surface by chemical functionalization or by attaching suitable nanostructures. This makes the nanotubes either more reactive and soluble or addressable and easier to manipulate. Therefore numerous publications deal with very different approaches to achieve this goal.[1] Various promising techniques were reported that lead to homogeneous tube coatings.[2−5] For further fundamental studies of the behavior of carbon nanotubes, it is of tremendous interest to develop techniques allowing the deliberate modification of well-specified sites on the nanotube.[6] In this context, the dissymmetric attachment of nanoobjects to one end of a nanotube deserves particular attention. Dissymmetric functionalization of micro- and nanoobjects is of major importance to study, for example, directed self-assembly, but also for many applications ranging from molecular electronics to sensing and catalysis. Various approaches to generate dissymmetric particles have been reported in the recent literature. These Janus-type particles have been obtained either by protection/deprotection mechanisms,[7] focused laser-induced reactions,[8] cojetting of parallel polymer solutions under the influence of an electrical field,[9] anisotropic electroless deposition,[10] or with microfluidic techniques.[11] However, so far most of the methods used to generate such objects need to break the symmetry by introducing interfaces like in the case of sputtering,[12,13] stamp coating,[14,15] and Langmuir−Blodgett-based techniques.[16] This makes the preparation of large quantities rather difficult. Thus, there is an increasing interest in developing alternative methods to replace the two-dimensional approaches by truly three-dimensional techniques allowing a scaleup of the production of Janus objects to larger quantities by using bulk procedures.[17] One interesting approach with respect to this challenge is based on a process using particle-stabilized wax emulsions to chemically modify the two sides of an object in a different way.[18] Another very attractive and complementary method that uses the concept of bipolar electrochemistry[19] has been reported by Bradley et al. and allows generating metal layers in a dissymmetric way on different substrates.[20,21] This approach can be used at the submicrometer scale,[22] but so far it is very difficult to carry out similar experiments with nanoscale objects because in this case very high electric fields have to be applied. The related problems can be overcome following an approach that we describe in the present contribution. We demonstrate that the concept of bipolar electrochemistry can be easily adapted to generate dissymmetric metal-modified carbon nanotubes in an aqueous bulk phase when using a simple capillary electrophoresis setup. In this case the capillary electrophoresis setup serves like a reaction chamber for an inorganic synthesis, analogous to what has been also reported for biochemical reactions.[23]

In general, bipolar electrochemistry occurs when an external electrical field polarizes an object that is not physically connected to the electrodes and thus generates

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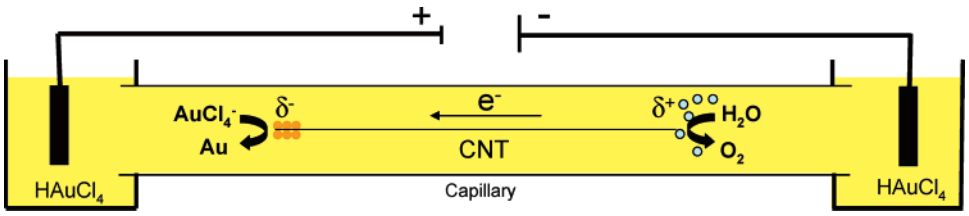

Figure 1. Capillary filled with an aqueous CNT/$AuCl_4^-$ suspension dipping in the two reservoirs of a capillary electrophoresis setup. A high electric field is applied, leading to the polarization of the individual nanotubes, thus triggering different electrochemical reactions on either end.

an anodic and a cathodic area on the same object.[24] The substrate can be any kind of material, but its conductivity must be higher than that of the surrounding medium. The induced potential difference between the two extremities of the object, and therefore the kinetics of the associated redox reactions, is directly proportional to the particle's effective length.[22] This becomes a major problem for a nanosized object, because in this case very high external voltages have to be applied to induce the necessary potential difference between the two sides of the object. It typically leads to the formation of gas bubbles in the reaction medium when working in aqueous electrolytes and thus induces convection that disturbs the orientation of the particles in the field. To avoid rotation, it is therefore necessary to immobilize the particles on a support and use organic solvents to increase the resistance of the electrolyte and the accessible potential window.[21] These are serious limitations because the experiment is then no longer a true bulk process, and furthermore from a practical point of view aqueous systems are preferable to organic solutions. With the present approach, it is possible to avoid these problems by using an experimental setup that is derived from capillary electrophoresis. A stabilized suspension of short carbon nanotube segments in an aqueous solution containing $AuCl_4^-$ is introduced in a glass capillary with the open ends dipping in the anodic and cathodic compartments of an electrochemical cell containing an aqueous solution of $HAuCl_4$ (see Figure 1).

When the capillary is exposed to a high electric field (10−30 kV), an electroosmotic flow is generated inside the capillary, transporting the CNT/$AuCl_4^-$ suspension from the anodic capillary inlet towards the cathodic compartment. Close to the cathodic outlet of the capillary, the absorbance of the passing-by solution can be monitored, thus allowing a measurement of the transient time. Because of the high field strength and the resulting laminar flow characteristic for such a setup, the nanotubes are aligned parallel to the potential gradient, thus generating an optimized potential drop between the two tube ends. This potential drop has to trigger the following two reactions:

Negatively polarized tube side: $AuCl_4^- + 3e \leftrightarrow Au$

$$E^\circ = +0.99 \text{ V}$$

Positively polarized tube side: $2H_2O \leftrightarrow O_2 + 4e + 4H^+$

$$E^\circ = +1.23 \text{ V}$$

From these thermodynamic values, one can conclude in a first order approximation that a potential difference of at least 240 mV is needed between the two tube ends. However, as these potentials are standard potentials and the experiment is conducted far from standard conditions in terms of concentrations and partial gas pressures, large deviations from this threshold value can be expected. Consequently, we decided to first perform a proof-of-principle experiment to evaluate this threshold value with a setup analogous to the capillary electrophoresis but at a larger scale in terms of capillary diameter and size of the modified objects to allow an optical observation of the ongoing metal deposition. A 1 mm long carbon fiber was inserted into a glass capillary connected to two reservoirs filled with $HAuCl_4$ electrolyte. The fiber was observed under the microscope during the application of different potential values. It was found that potentials higher than 40 V are needed to generate a visible metal deposit on the cathodic side of the fiber (see Figure 2).

After less than 5 min, a visible gold deposit was clearly formed on the negatively polarized end of the fiber. In the course of 1 h, the metal continued growing and its morphology, as revealed by scanning electron microscopy (see Supporting Information), was dominated by an agglomeration of small crystallites. According to the above equations, oxygen should evolve on the right-hand side of the fiber. However, no bubble formation was observed in this experiment, because the reaction rate was slow enough to allow the produced oxygen to dissolve in the electrolyte and diffuse away from the fiber. If an identical experiment is performed at much higher voltages, the reaction rate would become high enough to allow local oversaturation of the electrolyte with oxygen, and therefore visible bubble formation would occur at the anodic extremity of the fiber (see Supporting Information). In such a case, there is a risk that the experiment would spontaneously stop after a few minutes because the bubbles would fill the entire capillary and prevent current flow.

From these preliminary results, we can roughly calculate that a potential difference of at least 500 mV between the two ends of the fiber is necessary to trigger the bipolar process. Extrapolating the value to an experiment with 1000× shorter objects like nanotubes results in an overall voltage of 50 kV for a 10 cm long capillary (see Supporting Information). This value is within the order of magnitude of voltages typically used in capillary electrophoresis and can also still be decreased by using solutions with a lower electrolyte concentration. This result encouraged us to perform an analogue experiment with a stabilized suspension

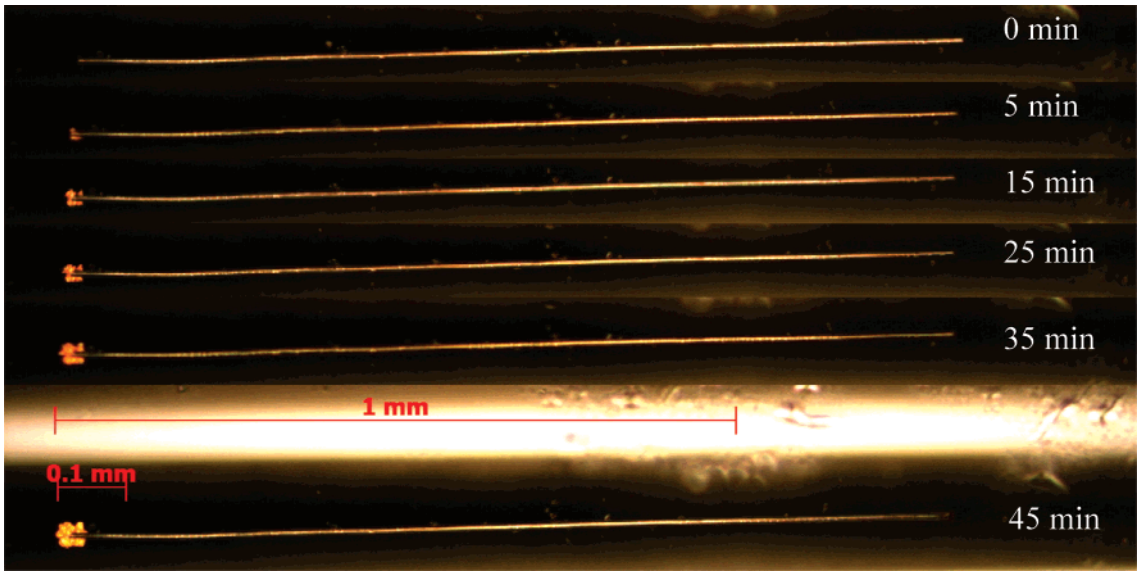

Figure 2. Optical micrographs of a carbon fiber inside a glass capillary during dissymmetric gold deposition by bipolar electrochemistry. The applied voltage was 70 V for a capillary with a length of 10 cm, filled with 10 mM $HAuCl_4$ aqueous electrolyte.

of multiwall carbon nanotubes (MWCNT). The aqueous MWCNT suspensions were prepared following a straight forward procedure that we recently proposed for the solubilization of different types of carbon.[25,26] In brief, the MWCNT raw material was treated with ultrasound in the presence of an aqueous solution of polyoxometalates. These molecules have a very high affinity for carbon[27] and tend to chemisorb on defect sites of the CNTs, leading to an overall negative charge of the CNTs, making them dispersible in water. When high-power ultrasound was used, the CNTs were simultaneously shortened and quite well-defined nanotubes with a narrower size distribution were obtained. Such a suspension was mixed with $HAuCl_4$, and the capillary of a commercially available electrophoresis equipment was filled with this solution. Then, both ends of the capillary were dipped in an aqueous $HAuCl_4$ solution (1 mM), and the voltage was applied. The CNT retention time can be measured by following the absorbance close to the outlet of the capillary. A decrease in absorbance indicated that all the CNTs have left the capillary. Typical retention times were of the order of minutes and usually the electrophoresis experiment was stopped just 20 s before all CNTs had left to collect the fraction of CNTs having spent a maximum time in the capillary (see Supporting Information). The sample was directly collected on a transmission electron microscopy (TEM) grid and washed three times with distilled water to remove $HAuCl_4$, which disturbs the imaging. Figure 3 shows a set of such images, typically obtained with the described procedure.

When very concentrated suspensions of CNTs are used, the sample collected on the TEM grid is characterized by entangled nanotubes (Figure 3A). Some tubes are modified with a gold deposit at one end, but there are also unmodified CNTs. Unmodified nanotubes seem to exist only within such aggregates, whereas when the tubes are individual they are almost always modified (see below). Most likely, being entrapped and in electrical contact with other nanotubes in an aggregate changes completely the potential distribution for every nanotube, and thus the conditions for efficient bipolar electrodeposition are not fulfilled for all CNTs. Besides that, there are several other possible origins for a nonquantitative modification yield. First of all, the gold deposit can detach from the tube during the collection and rinsing procedure, as it seems to be the case for the small side tube in Figure 3B. Second, nanotubes can be more or less conducting depending on their morphology and defects. In the extreme case of an isolating tube, no deposition can occur and even for conducting tubes the conductivity has to be better than that of the surrounding electrolyte to induce a sufficient potential difference. The third reason is that the potential drop scales with the length of the tube, and therefore shorter tubes might experience a potential difference between the two ends that is below the threshold value. A nice illustration of this effect can be seen in Figure 3C, allowing a direct comparison of the amount of gold deposit as a function of tube length under otherwise identical conditions. The long tube experienced a bigger potential difference, and therefore the electrodeposition kinetics is faster than that for the short tube shown in the lower right corner, which has only a very small gold cluster at its tip. The average size of the deposit can be varied by changing the total voltage and the length of the capillary, because this changes not only the potential drop between the two ends of the nanotube, but also the time it takes to travel through the capillary and therefore the overall reaction time.

When the initially injected suspension is more diluted, to avoid aggregation of the CNTs in the capillary and also clogging of the capillary entrance, the final density of nanotubes on the TEM grid is sufficiently low to allow imaging of individual modified tubes (Figure 3D−F). A well-defined deposit can be seen in all cases, and it is specifically located only at one end of the CNT, indicating that the tube must have passed the capillary without changing orientation with respect to the electric field. The chemical nature of the

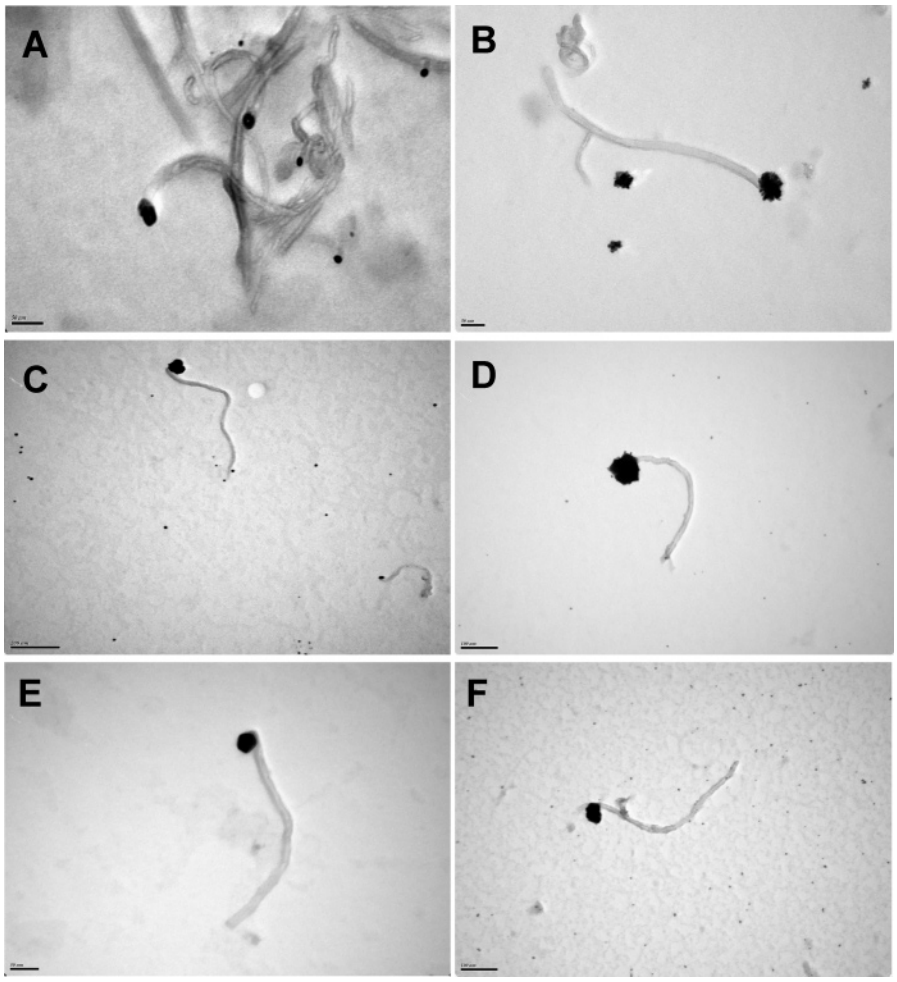

Figure 3. Examples of different CNT samples modified on one end with a gold deposit in a solution of 1 mM $HAuCl_4$ performing bipolar electrochemistry in a 45 cm long capillary under 30 kV. (Scale bar is 200 nm (C), 100 nm (D,F), 50 nm (A,B,E)).

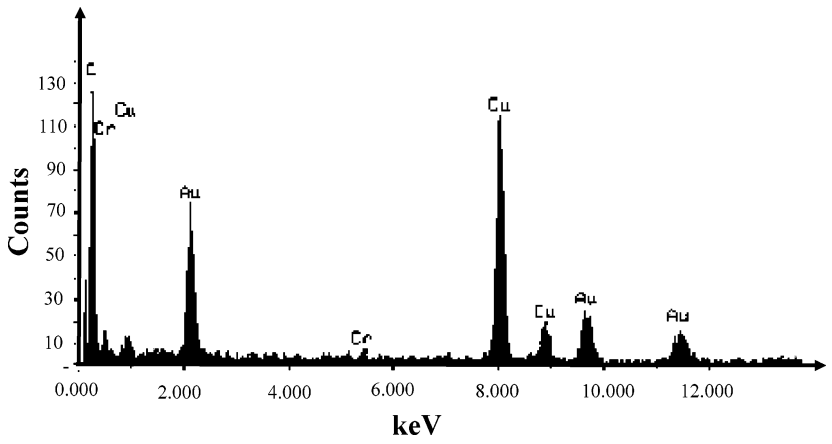

Figure 4. EDX characterization of the chemical composition of the particle attached to one end of a nanotube. Carbon, copper, and chromium peaks are part of the background signal originating from the TEM grid.

deposit has been checked for several samples and could be confirmed as being gold (Figure 4). As the samples were collected on TEM grids, the composition of the latter (carbon on copper mesh) interferes with the characterization, but a prominent gold signal can still be clearly seen.

In summary, the concept of bipolar electrochemistry has been adapted to modify in a dissymmetric way multiwall carbon nanotubes with a gold cap. The method employed to create these Janus-type objects is based on a slightly modified capillary electrophoresis experiment, (i) allowing the application of the mandatory high voltages (ii) without having to use organic solvents and (iii) especially avoiding gas bubble formation in the reaction chamber, which otherwise would completely prevent the alignment of the nanotubes in the

electric field. Most importantly, the procedure uses a real bulk-phase reaction in contrast to most of the literature methods based on interfaces to break the symmetry. This makes the method very attractive to scale-up the production of such dissymmetric objects.

Looking to the future, this capillary assisted bipolar electrodeposition (CABED) can be generalized to other types of nanoobjects and also deposits of a very different nature such as other metals, semiconductors, or polymers. The approach therefore opens up the way to a whole new family of experiments leading to complex nanoobjects with an increasingly sophisticated design allowing original applications like the recently proposed corked nano test tubes.[28,29] In addition, the procedure reported here could also be adapted to sort conducting, semiconducting, and isolating carbon nanotubes, as the latter ones will not be modified with metal, whereas the first two categories of species will undergo a potential dependent metal modification.

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Supporting Information Available: Supporting information is available concerning more detailed experimental conditions as well as the characterization of the gold deposit microstructure, the oxygen evolution at the anodic end of the fibres and the variation of absorbance as a function of time at the outlet of the capillary. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Balasubramanian, K.; Burghard, M. *Small* **2005**, *1*, 180.
(2) Rahmann, G. M. A.; Guldi, D. M.; Zambon, E.; Pasquato, L.; Tagmatarchis, N.; Prato, M. *Small* **2005**, *1*, 527.
(3) Jiang, K.; Eitan, A.; Schadler, L. S.; Ajayan, P. M.; Siegel, R. W.; Grobert, N.; Mayne, M.; Reyes-Reyes, M.; Terrones, H.; Terrones, M. *Nano Lett.* **2003**, *3*, 275.
(4) Liu, L.; Wang, T.; Li, J.; Guo, Z.-X.; Dai, L.; Zhang, D.; Zhu, D. *Chem. Phys. Lett.* **2003**, *367*, 747.
(5) Ellis, A. V.; Vijayamohanan, K.; Goswami, R.; Chakrapani, N.; Ajayan, P. M.; Ramanath, G.; Ramanathan, L. S. *Nano Lett.* **2003**, *3*, 279.
(6) Cui, J. B.; Burghard, M.; Kern, K. *Nano Lett.* **2002**, *2*, 117.
(7) Perro, A.; Reculusa, S.; Pereira, F.; Delville, M.-H.; Mingotaud, C.; Duguet, E.; Bourgeat-Lami, E.; Ravaine, S. *Chem. Comm.* **2005**, *44*, 5542.
(8) Hugonnot, E.; Delville, M.-H.; Delville, J.-P. *Appl. Surf. Sci.* **2005**, *248*, 470.
(9) Roh, K.-H.; Martin, D. C.; Lahann, J. *Nat. Mater.* **2005**, *4*, 759.
(10) Cui, J.-Q.; Kretzschmar, I. *Langmuir* **2006**, *22*, 8281.
(11) Nisisako, T.; Torii, T.; Takahashi, T.; Takizawa, Y. *Adv. Mater.* **2006**, *18*, 1152.
(12) Takei, H.; Shimizu, N. *Langmuir* **1997**, *13*, 1865.
(13) Lu, Y.; Xiong, H.; Jiang, X.; Xia, Y.; Prentiss, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **2003**, *125*, 12724.
(14) Cayre, O.; Paunov, V. N.; Velev, O. D. *J. Mater. Chem.* **2003**, *13*, 2445.
(15) Paunov, V. N.; Cayre, O. J. *Adv. Mater.* **2004**, *16*, 788.
(16) Fujimoto, K.; Nakahama, K.; Shidara, M.; Kawaguchi, H. *Langmuir* **1999**, *15*, 4630.
(17) Hong, L.; Cacciuto, A.; Luijten, E.; Granick, S. *Nano Lett.* **2006**, *6*, 2510.
(18) Hong, L.; Jiang, S.; Granick, S. *Langmuir* **2006**, *22*, 9495.
(19) Fleischmann, M.; Ghoroghchian, J.; Rolison, D.; Pons, S. *J. Phys. Chem.* **1986**, *90*, 6392.
(20) Bradley, J.-C.; Chen, H.-M.; Crawford, J.; Eckert, J.; Ernazarova, K.; Kurzeja, T.; Lin, M.; McGee, M.; Nadler, W.; Stephens, S. G. *Nature* **1997**, *389*, 268.
(21) Bradley, J.-C.; Zhongming, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 1663.
(22) Bradley, J.-C.; Babu, S.; Ndungu, P. *Fullerenes, Nanotubes, Carbon Nanostruct.* **2005**, *13*, 227.
(23) Berezovski, M.; Drabovich, A.; Krylova, S. M.; Musheev, M.; Okhonin, V.; Petrov, A.; Krylov, S. N. *J. Am Chem. Soc.* **2005**, *127*, 3165.
(24) Ndungu, P. G. Ph.D. Thesis, Drexel University, PA, 2004.
(25) Garrigue, P.; Delville, M.-H.; Labrugère, C.; Cloutet, E.; Kulesza, P. J.; Morand, J. P.; Kuhn, A. *Chem. Mater.* **2004**, *16*, 2984.
(26) Fattakhova, D.; Kuhn, A. *Carbon* **2006**, *44*, 1942.
(27) Kuhn, A.; Anson, F. C. *Langmuir* **1996**, *12*, 5481.
(28) Gasparac, R.; Kohli, P.; Mota, M. O.; Trofin, L.; Martin, C. R. *Nano Lett.* **2004**, *4*, 513.
(29) Hillebrenner, H.; Buyukserin, F.; Kang, M.; Mota, M. O.; Stewart, J. D.; Martin, C. R. *J. Am Chem. Soc.* **2006**, *128*, 4236.

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