J. Phys. Chem. A **1998,** *102,* 4411−4413

Scanning Tunneling Microscopy of Ring-Shape Endohedral Metallofullerene $(Nd@C_{82})_{6,12}$ Clusters

Nian Lin,*,† Houjin Huang,‡ Shihe Yang,‡ and Nelson Cue†

Department of Physics, and Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

Received: January 30, 1998; In Final Form: April 1, 1998

Endohedral metallofullerene molecules of the type $Nd@C_{82}$ were deposited on thin films of C_{60} and investigated with an ultrahigh vacuum scanning tunneling microscope (UHV-STM). The as-deposited $Nd@C_{82}$ are observed to form well-ordered two-dimensional close-packed structures. These structures are transformed to very stable ring-shape clusters of $(Nd@C_{82})_n$ after they experienced a strong electric field of the scanning. The ring-shape clusters have a shape of a hexagonal polygon, consisting of either 6 or 12 molecules, and this points to the formation of covalently bonded $Nd@C_{82}$ supramolecules.

Introduction

Endohedral metallofullerenes were proposed and produced soon after the discovery of C_{60}.[1−8] A variety of experimental methods have shown that a group-3 metal (M = Sc, Y, La) or lanthanide metal atom can be encapsulated in a fullerene C_{82} molecule to make an endohedral metallofullerene $M@C_{82}$.[3−8] The M ion is found to have a valence of +3, indicating the transfer of three electrons to the carbon cage, and to be located off-center.[9−13] Because of these, $M@C_{82}$ is expected to have a permanent dipole moment.[13] The net charge on the metal ion was found to change little when $M@C_{82}$ loses or accepts an electron, implying that the endohedral metallofullerenes are composed of a positively charged kernel metal and a negatively charged cage.[14] Thus, many expect that the +3 charged metal ions make endohedral metallofullerenes molecules behave like Li atoms, in which case, two electrons are paired with each other and the remaining one gives rise to a singly occupied molecular orbital (SOMO). An ab initio calculation of an isolated $La@C_{82}$ molecule showed that the SOMO is delocalized over the carbon cage.[13] Nevertheless, available experimental evidence has shown that the intermolecular interaction of endohedral metallofullerenes is primarily a dipole−dipole interaction with no strong chemical bonds involved.[13,15]

Our previous STM studies[16,17] have revealed that endohedral metallofullerene $Nd@C_{82}$ molecules form well-ordered two-dimensional close packing while they are deposited on a substrate of C_{60} films (overlaying a freshly cleaved HOPG surface). This suggests that an intermolecular force at play is a dipole−dipole interaction, which is relatively weaker than that of a covalent bonding. In this Letter, we report a STM-tip driven transition of $Nd@C_{82}$ molecules from the close-packed configurations to ring structures that have never been reported before. We find that the relatively weakly bound close-packed structures are reconfigured by the high bias-voltage of the STM tip during scanning. When this voltage exceed a critical value of about 4 V, we observed mainly ring-shaped clusters consisting of either 6 or 12 $Nd@C_{82}$ molecules. The high stability of these rings suggests that the $Nd@C_{82}$ molecules are covalently bonded together analogous to the case of CH in benzene.

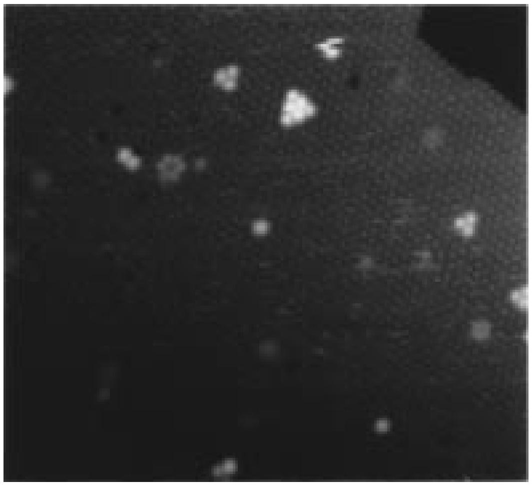

Figure 1. STM image of $Nd@C_{82}$ molecules (bright spheres) on a crystalline C_{60} substrate. The scale is provided by noting that the lattice constant of C_{60} substrate is 1.0 nm. Tunneling current is 30 pA, and bias voltage is 2.0 V (applied to the sample).

Experimental Aspects

The preparation of the $Nd@C_{82}$ samples and the setup for their in-situ study with an UHV-STM have been described in our previous publications.[8,16] The purity of the samples as measured by mass spectrometry is over 99.9%. Briefly, the experimental procedure is to deposit in an UHV chamber at a low rate the $Nd@C_{82}$ molecules onto a crystalline C_{60} film overlaying a freshly cleaved HOPG substrate. The sample is later transferred to another UHV chamber for STM characterization without breaking the vacuum.

Images taken at a scanning bias voltage of 2.0 V, with the positive potential applied to the sample, are consistently reproducible and show well-ordered configurations. Figure 1 shows a typical result obtained at low-deposition rate. $Nd@C_{82}$ molecules are seen to aggregate into close-packed configurations as dimers, trimers, and so forth. However, once the bias voltage

---

[*] Corresponding author. Present address: Department of Physics and Measurement Technology, Linköping University, S-581 83, Linköping, Sweden. E-mail address: niali@ifm.liu.se.

[†] Department of Physics.

[‡] Department of Chemistry.

S1089-5639(98)00960-8 CCC: $15.00

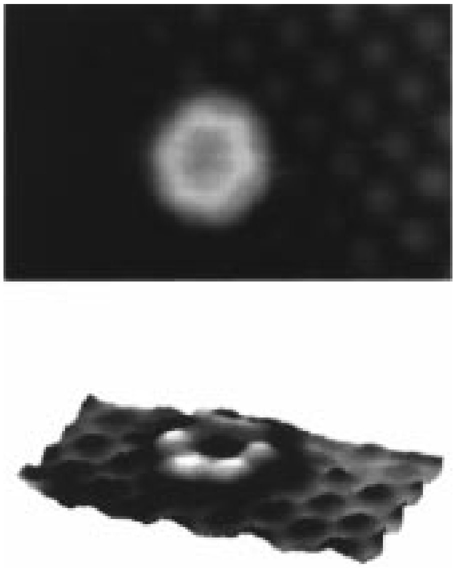

Figure 2. High-resolution STM images of two rings. Top figure is in two dimensions, while the bottom one is in three dimensions. Tunneling current is 30 pA, and bias voltage is 2.0 V (applied to the sample).

is increased above a critical value, both positive and negative relative to the sample, these configurations are changed dramatically while the underlying C_{60} lattice exhibits no discernible disturbance. The lowest bias voltage to incite the reconfiguration is 2.5 V. This phenomenon indicates that the Nd@C_{82} molecules are sensitive to the external electric field applied by the tip. It is known that the electric field around a sharp tip is highly inhomogeneous, and the strongest field is at the apex of the tip. Therefore, a reconfiguration will occur once the electric field of the tip is strong enough to overcome the forces that bind Nd@C_{82} molecules together. At a typical tip-to-sample distance of 1 nm, the electric field near the tip apex at 2.5-V bias will be over 2.5×10^9 V/m. In such a field, the Nd@C_{82} molecules having a dipole moment of 4 D will have a dipole energy of about 180 meV. This energy is much larger than the cohesive energy of Nd@C_{82} estimated from the dipole−dipole attraction picture. Thus, the electric field between the tip and sample is capable of provoking a reconfiguration. On the other hand, this dipole−dipole energy is smaller than that of a typical covalence bond. So, the tip-induced reconfiguration implies the absence of strong covalent chemical bond among the Nd@C_{82} molecules in the as-deposited phase. It should be noted that the inhomogeneous field of the tip affected little if at all the nonpolar C_{60} molecules, and so, the C_{60} lattice was not disturbed by this electric field. We find that further increasing the bias voltage to 3.2 V will lead to the formation of ring-shape clusters. Such features have never been observed before the application of high bias scanning. These ring-shape clusters appear repeatedly after the tip reconfiguration on all the samples deposited with Nd@C_{82}, while they are totally absent on the samples without Nd@C_{82}.

Results and Discussion

Figure 2 shows high-resolution images of two such ring-shape clusters. Clearly evident is a hexagonal polygon formed with six Nd@C_{82} molecules. The ring has an inner diameter of 1.0 ± 0.2 nm, an outer diameter of 3.0 ± 0.2 nm, and a height of 1.2 ± 0.5 nm. The nearest-neighbor (NN) distance in a ring is 0.9 nm on average, and this is shorter than the 1.2-nm NN length observed for the close-packed structures before reconfiguration. Our STM observations reveal that rings always consist of 6 or 12 molecules. In other words, no ring of other numbers, for example, five or seven, has ever been seen. Moreover, all rings are complete, and no partial rings seem to exist. Unlike the close-packed Nd@C_{82} configurations of dimers or trimers, the rings cannot be reconfigured by the scanning tip even on when the bias voltage is raised higher. The attempts to reshape the rings back to dimers or trimers have never succeeded. The rings can survive a bias as high as 4.5 V, which is the limit for obtaining stable STM images for our setup.

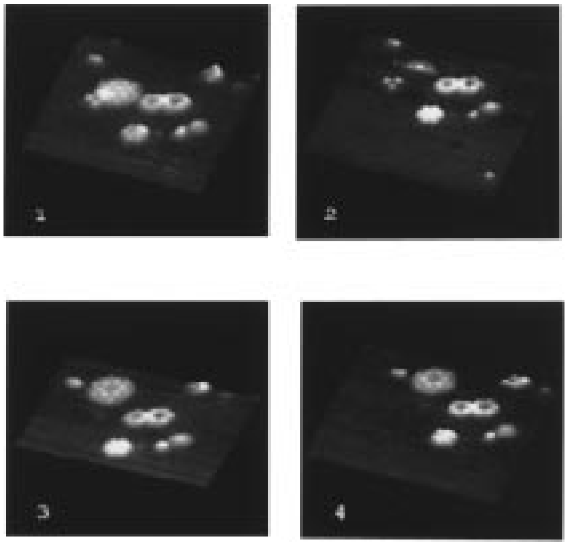

Figure 3. Four STM images scanned over the same area obtained sequentially in time showing the motion of a ring. Tunneling current is 30 pA, and bias voltage is 2.0 V (applied to the sample).

The rings can be moved by the tip as a whole unit without changing their structures. Figure 3 shows such a ring-moving process. The four images 1, 2, 3, and 4 correspond to the same area scanned sequentially in time. The first scan shows a 12-number "big" ring, a 6-number ring, and 2 interconnected rings. An extra Nd@C_{82} molecule is seen to occupy the center of the "big" ring. While scanning the second image, a bias pulse of 4.0 V was applied accidentally when the tip was over the "big" ring, and this pulse lasted 0.1 s. As a result, only the upper part of the "big" ring is seen in the second image, while the other rings are unchanged except that an extra Nd@C_{82} molecule has filled the hollow center of the six-number ring. Parts 3 and 4 of Figure 3 are images taken by scanning at 2.0-V bias, and the two are almost identical. However, one can see that the "big" ring moves upward and loses the extra center molecule, while its ring-shape structure remains unchanged. From this group of images, we learn that (1) the center site of the rings easily gains or loses a molecule, (2) the rings are weakly coupled to the underlying C_{60} substrate, and (3) molecules within a ring are bound to each other tightly.

Estimates show that the simple dipole−dipole interaction picture cannot explain the stability of the rings. Suppose that the molecules within a ring are bonded by a dipole−dipole interaction. The calculated total dipole energy for a six-number ring has a value less than 270 meV. This means that a tip-to-sample bias of about 3.7 V would be able to break up the ring. But this is contrary to the experimental observations. Also, there are other considerations that suggest a different type of intermolecular interaction for the rings: (1) the NN length between Nd@C_{82} molecules within a ring is only ∼0.9 nm, much shorter than the equilibrium distance expected for van der Waals interactions (∼1.2 nm); (2) the rings are very stable and can be dragged across the surface without changing their structures; (3) the rings always consist of 6 or 12 molecules, which implies 6 as a magic number; (4) the rings prefer to have a hexagonal shape. Perhaps the open-shell SOMO character of the M@C_{82} molecules[13] may induce covalent bonding among the Nd@C_{82} molecules. A covalent bond picture would explain well the salient features of our experimental observations. The short intermolecular distance is consistent with the charge transfer between molecules, and the high stability with the strong intermolecular binding. The magic number, the completeness of the rings, and the preferred spatial configurations are typical characters of covalent bonded structures. Furthermore, the saturated nature of the covalent interaction permits the addition or removal of an extra molecule at the center site of the rings with relative ease. All these suggest to us that the rings are really very stable supramolecules of Nd@C_{82} of the form (Nd@C_{82})$_n$, with $n = 6$ or 12.

The close-packed arrangement of the Nd@C_{82} molecules on initial adsorption is easy to understand because their aggregation is governed mainly by the kinetics. Since the deposition rates are very low, these molecules reach the surface one by one. They will join together when they encounter each other and result in close-packed configurations. On the other hand, rings are formed by the participation of at least six molecules and in the presence of a strong inhomogeneous electric field. Such a situation is totally different from the initial conditions of adsorption. Hence, we propose that the initially formed close packing is a metastable state while the rings correspond to a more stable state. To accomplish the transformation, the initial structures formed on adsorption have to be broken up by the high bias voltage of the tip so that the Nd@C_{82} molecules can be set free. These freed molecules then recombine to form covalent bound supramolecules in the presence of the strong external electric field.

Conclusion

New aggregation behaviors of endohedral metallofullerene Nd@C_{82} molecules deposited at a low coverage on C_{60} films are revealed in our study using a UHV-STM. These Nd@C_{82} molecules initially form close-packed configurations expected of the dipole interactions among the molecules that have a permanent dipole moment. These are transformed to very stable ring-shape clusters after they experienced a high bias-voltage scanning by the STM tip. Each of these rings consists of 6 or 12 molecules. The ring molecules is actually a hexagonal polygon of 3.0 nm in outer diameter. Their stability under strong external fields, small intermolecular distance (~0.9 nm), and preferred shape indicate an interaction distinct from the simple dipole−dipole attraction. Charge transfer among the molecules is likely to occur and will result in a covalent bonding that gives rise to the observed supramolecular rings (Nd@C_{82})$_n$.

Acknowledgment. The work is supported in part by grants, HKUST 637/94P and HKUST 601/95P, awarded by the Research Grants Council of the Hong Kong Government.

References and Notes

(1) Heath, J. R.; O'Brien, S. C.; Zhang, Q.; Liu, Y.; Curl, R. F.; Kroto, H. W.; Tittel, F. K.; Smalley, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 7779.

(2) Chai, Y.; Guo, T.; Jin, C.; Haufler, R. E.; Chibante, L. P. F.; Fure, J.; Wang, L.; Alford, J. M.; Smalley, R. E. *J. Phys. Chem.* **1991**, *95*, 7564.

(3) Johnson, R.D; De Vries, M. S.; Salem, J.; Bethune D. S.; Yannoni, C. S. *Nature* **1992**, *355*, 239.

(4) Weaver, J. H.; Chai, Y.; Kroll, G. H.; Jin, C.; Ohno, T. R.; Haufler, R. E.; Guo, T.; Alford, J. M.; Palmer G.; Smalley, R. E. *Chem. Phys. Lett.* **1992**, *190*, 460.

(5) Shinohara, H.; Sato, H.; Ohkohchi, M.; Ando, Y.; Kodama, T.; Shida, T.; Kato T.; Saito, Y. *Nature* **1992**, *357*, 52.

(6) Ding, J. Q.; Yang, S. H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2234.

(7) Ding, J. Q.; Yang, S. H. *J. Am. Chem. Soc.* **1996**, *118*, 11254.

(8) Ding, J. Q.; Lin, N.; Weng, L. T.; Cue, N.; Yang, S. H. *Chem. Phys. Lett.* **1996**, *261*, 92.

(9) Hino, S.; Takahashi, H.; Iwasaki K.; Matsumoto, K. *Phys. Rev. Lett.* **1993**, *71*, 4261.

(10) Moro, L.; Ruoff, R. S.; Becker, C. H.; Lorents D. C.; Malhotra, R. *J. Phys. Chem.* **1993**, *97*, 6801.

(11) Bandow, S.; Kitagawa, H.; Mitani, T.; Inokuchi, H.; Saito, Y.; Yamaguchi, H.; Hayashi, N.; Sato, H.; Shinohara, H. *J. Phys. Chem.* **1992**, *96*, 9609.

(12) Yannoni, C. S.; Hoinkis, M.; de Varies, M. S.; Bethune, D. S.; Salem, J.; Crowder, M. S.; Johnson, R. D. *Science* **1992**, *256*, 1191.

(13) Poirie, D. M.; Knupfer, M.; Weaver, J. H.; Andreoni, W.; Laasonen, K.; Parrinello, M.; Bethune, D. S.; Kikuchi K. Achiba, Y. *Phys. Rev. B.* **1994**, *49*, 17403.

(14) Nagase, S.; Kobayashi, K. *J. Chem. Soc., Chem. Commun.*, **1994**, *16*, 1837.

(15) Shirohara, H.; Inakuma, M.; Kishida, M.; Yamazaki, S.; Hashizume T.; Sakurai, T. *J. Phys. Chem.* **1995**, *99*, 13690.

(16) Lin, N.; Ding, J. Q.; Yang, S. H.; Cue, N. *Phys. Lett. A.* **1996**, *222*, 190.

(17) Lin, N.; Huang, H.; Yang. S. H.; Cue, N. Submitted.