Supporting Information for

Formation of Superatom Monolayer Using Gas-Phase-Synthesized Ta@Si$_{16}$ Nanocluster Ions

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1. Effect of $V_{\text{tip}}$ on the dot height measured by STM on dots/C$_{60}$ and dots/6T

In the main text, we discussed the geometry of Ta@Si$_{16}$ nanoclusters adsorbed on thin films of C$_{60}$ and 6T molecules using the heights of dots created by depositing Ta@Si$_{16}$ cations onto both molecular films, where each dot height was estimated as the difference in height of the STM tip between the tops of the dot and the molecules. Since the tip height difference between adsorbates and surfaces in STM images is generally affected by the difference in the electrical density of states (DOS) between them, there is a possibility that the heights of dots on molecular films fluctuate depending on the tip bias voltage ($V_{\text{tip}}$). Therefore, the effect of the value of $V_{\text{tip}}$ on the dot height ($h_d$) should be investigated before discussing the geometry of Ta@Si$_{16}$ nanoclusters.

In the case of Ta@Si$_{16}$/C$_{60}$, the height difference between the Ta@Si$_{16}$ nanocluster and C$_{60}$ molecules in the filled-state imaging ($V_{\text{tip}} > 0$) would be observed to be higher than the original height difference, particularly, in the range of $V_{\text{tip}}$ from ~0.5 V to ~2.2 V. This is because C$_{60}$ molecules exhibit a large energy gap in the filled state, as shown in Fig. 4f in the main text, whereas the Ta@Si$_{16}$ nanocluster shows a clear peak in the DOS at $V_{\text{tip}}$ of ~1.0 V, as shown in the Fig. 4c, 4d, and 4e. In contrast, in the empty state ($V_{\text{tip}} < 0$), the difference in electronic structure between the Ta@Si$_{16}$ nanocluster and the C$_{60}$ molecule is clearly smaller than that in the filled state. Of course, since the electronic DOS in the empty state of the Ta@Si$_{16}$ nanocluster does not completely agree with that of C$_{60}$ molecules, there is a possibility that the height of dots on C$_{60}$ films fluctuates with the value of $V_{\text{tip}}$. However, our additional result indicates that this fluctuation is negligible, as follows. The black, blue, and red curves in Fig. S1b show STM height profiles taken at $V_{\text{tip}}$ of -2.3 V, -2.0 V, and -1.7 V, respectively, which intersect the same three dots with $h_d$ of ~0.7 nm, ~0.8 nm, and ~0.85 nm, as indicated by the dotted blue line in Fig. S1a. In these profiles, the heights of the three dots are independent of the value of $V_{\text{tip}}$, strongly indicating that the difference in the electronic DOS between the Ta@Si$_{16}$ nanocluster and the C$_{60}$ molecule has a negligible impact on the height difference between them in empty-state imaging. Therefore, it is concluded that the geometry of Ta@Si$_{16}$/C$_{60}$ can be safely discussed on the basis of the dot-height histograms shown in Fig. 1f and 1g in the main text.

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**Fig. S1.** (a) STM image of C$_{60}$/HOPG taken after depositing Ta@Si$_{16}$ cations. (b) Cross-sectional line profiles taken along the blue line in (a) at $V_{\text{tip}}$ of -2.3 V (black), -2.0 V (blue), and -1.7 V (red).
Fig. S2a, S2b, and S2c show histograms of $h_d$ measured on dots/6T from STM height profiles taken at $V_{\text{tip}}$ of 1.7 V, -1.4 V, and -1.6 V, respectively. These results clearly indicate that the dot height distribution of dots/6T does not sensitively fluctuate with the value of $V_{\text{tip}}$, allowing us to conclude that the geometry of Ta@Si$_{16}$/6T can also be safely discussed on the basis of the histogram shown in Fig. 3c in the main text.

![Histograms of dot heights measured on the dots/6T from STM height profiles taken at $V_{\text{tip}}$ of 1.7 V, -1.4 V, and -1.6 V, respectively.](image)

Fig. S2. (a-c) Histograms of dot heights measured on the dots/6T from STM height profiles taken at $V_{\text{tip}}$ of +1.7 V, −1.4 V, and −1.6 V, respectively.

2. Deposition of Ta@Si$_{16}$ cations onto C$_{60}$-terminated HOPG with higher kinetic energy

We have investigated the effect of nanocluster fragmentation or deformation on dot formation in the deposition of Ta@Si$_{16}$ cations onto C$_{60}$-terminated surfaces. To intentionally induce fragmentation or deformation on surfaces, Ta@Si$_{16}$ cations were deposited onto a C$_{60}$-terminated HOPG surface with a kinetic energy ($E_k$) of ~1.25 eV/atom, which is ~20 times larger than that used to obtain the samples shown in Fig. 1a–1d, 1f, and 1g in the main text. As a result, dots with $h_d < 0.45$ nm were mainly created, as shown in Fig. S3a and S3b. The formation of dots with $h_d < 0.45$ nm was considered to come from the deformation and/or fragmentation of Ta@Si$_{16}$.
nanoclusters on the surface, because such small values of $h_d$ cannot be explained by the adsorption of Ta@Si$_{16}$ nanoclusters. In contrast, the small dots with $h_d < 0.45$ nm are minor products in the deposition of Ta@Si$_{16}$ cations with a smaller $E_k$ of $\sim$0.01 eV/atom, as shown in Fig. 1f and 1g, also suggesting that the fragmentation or deformation of Ta@Si$_{16}$ nanoclusters hardly occurs in the low-energy deposition of cations.

Fig. S3. (a) STM image of C$_{60}$/HOPG surface taken after depositing Ta@Si$_{16}$ cations with $E_k$ of $\sim$1.25 eV/atom. (b) Cross-sectional line profile taken along the blue line in (a).

3. Optimized structures and electronic properties of Ta@Si$_{16}$-C$_{60}$ complexes

To gain insights into the structural and electronic properties of Ta@Si$_{16}$ cations immobilized on C$_{60}$ monolayer films, geometrical optimizations of Ta@Si$_{16}$+0-C$_{60}$ complexes starting from several initial structures were performed with TURBOMOLE 6.4-6.5$^{1,2}$ at the level of the Perdew-Burke-Ernzerhof functional$^{3}$ using the resolution-of-identity approximation$^{4}$ and the def-SV(P) basis set$^{5}$ along with a scalar relativistic effective core potential for Ta$^{6}$. Geometric optimizations were continued until the vibrational frequency analysis showed no imaginary frequencies, along the largest of which when found the geometric structures are relaxed. Natural population analysis$^{7}$ was used to investigate the charge distributions in the complexes.

Fig. S4 shows the optimized structures of Ta@Si$_{16}$-C$_{60}$ complexes with cationic (a–c) and neutral (d–f) states, where the neutral states were optimized starting from the corresponding cation structures after their optimization. Representative structural parameters, relative total energies ($\Delta E$), HOMO–LUMO gaps ($E_g$), and natural charges of Ta@Si$_{16}$ nanoclusters ($Q_{Ta@Si_{16}}$) are summarized in Table S1. For all the optimized structures of the Ta@Si$_{16}$-C$_{60}$ complexes, the Ta@Si$_{16}$
nanoclusters possess a fullerene structure having almost $D_{4d}$ symmetry, even when a Frank-Kasper (FK) structure having almost $T_d$ symmetry was given as the initial structure of the Ta@Si$_{16}$ nanoclusters (Fig. S4c). Some structures starting from $^{FK}$Ta@Si$_{16}$-C$_{60}$ (not shown here) result in separate configurations, i.e., covalent interconnection between Ta@Si$_{16}$ nanoclusters and C$_{60}$ molecules is not realized owing to the large bond length among nearest-neighbor Si and C atoms. This result suggests that individual $^{FK}$Ta@Si$_{16}$ cations are too stable to chemically bond with C$_{60}$ molecules. The formation of the $^{FK}$Ta@Si$_{16}$-C$_{60}$ complex via the increased intercluster distance may be one of the causes of the variation in height of the Ta@Si$_{16}$ nanoclusters on C$_{60}$ films reported in the text, although a detailed theoretical verification considering the van der Waals interaction between Ta@Si$_{16}$ nanoclusters and C$_{60}$ molecules is required, which is beyond the scope of the present study.

![Diagram](image)

**Fig. S4** Optimized structures of (a–c) [Ta@Si$_{16}$-C$_{60}$]$^+$ and (d–f) Ta@Si$_{16}$-C$_{60}$, where orange, black, and gray spheres represent Si, Ta, and C atoms, respectively.

To discuss the apparent height of Ta@Si$_{16}$/C$_{60}$ in the STM observation, the distance between the centers of the topmost C and Si atoms in the C$_{60}$ molecules and Ta@Si$_{16}$ nanoclusters ($h_2$ in Fig. S4), respectively, is first estimated as the height of the Ta@Si$_{16}$ nanoclusters. The value of $h_2$ varies from 7.2 to 8.1 Å among the complexes in their neutral and cationic states, in reasonable agreement with the experimental height of Ta@Si$_{16}$ nanoclusters on C$_{60}$ films shown in the main text. Furthermore, considering the difference in the van der Waals radii between Si (2.1 Å) and C (1.7 Å) atoms, the heights shown in Fig. 2 in the text were estimated by adding this difference (0.4 Å) to each value of $h_2$. 
In addition, regarding the charge state of the Ta@Si\textsubscript{16} nanocluster in the neutral Ta@Si\textsubscript{16}-C\textsubscript{60} complexes, it can be safely claimed that the Ta@Si\textsubscript{16} nanocluster tend to be positively charged as shown in Table S1, which supports the experimental results and the discussion in the text.

**Table S1.** Representative bond lengths and heights of C\textsubscript{60} molecules and Ta@Si\textsubscript{16} nanoclusters (\(h_1\) and \(h_2\), respectively, see Fig. S4) in Å, relative total energies (\(\Delta E\)), HOMO-LUMO gaps (\(E_g\)) in eV, and natural charges of Ta@Si\textsubscript{16} (\(Q_{TaSi@16}\)) and C\textsubscript{60} (\(Q_{C60}\)) for complexes a–f in Fig. S4.

<table>
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<th></th>
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<th>Si-Si</th>
<th>C-C</th>
<th>(h_1)</th>
<th>(h_2)</th>
<th>(\Delta E)</th>
<th>(E_g)</th>
<th>(Q_{TaSi16/C60})</th>
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<td>7.2</td>
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**References for Supporting Information**


