Supporting information for

Charge Transfer Complexation of Ta-Encapsulating $Ta@Si_{16}$ Superatom with C_{60}

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Index

S1. XPS measurements around C 1*s* core for Ta@Si_{16}/HOPG and HOPG

Figure S1 shows C 1*s* XPS spectra of HOPG before (black) and after Ta@Si_{16} deposition (red). Binding energy and peak width remained unchanged upon Ta@Si_{16} deposition, indicating the absence of chemical interactions between deposited Ta@Si_{16} and HOPG. Meanwhile, the C 1*s* peak changed by the deposition of Ta@Si_{16} upon C_{60} film due to the formation of the superatomic CT complex $(Ta@Si_{16})^{+}C_{60}^{-}$, as described in the main text (Fig. 2).

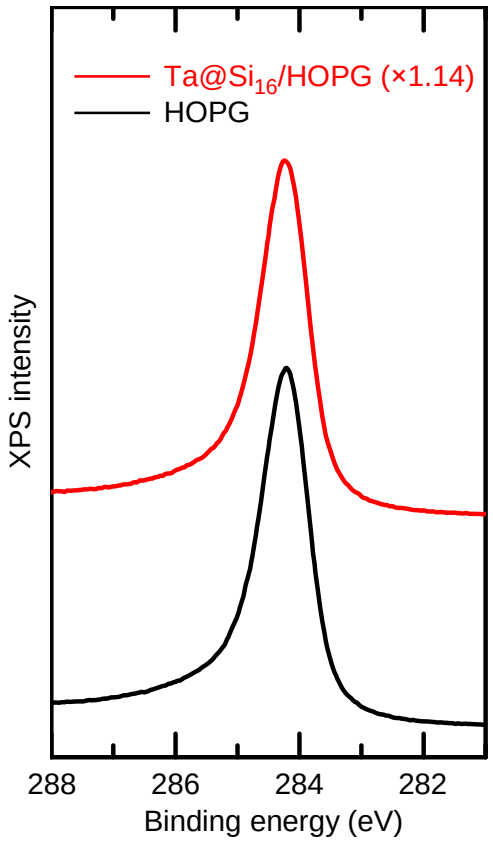

Figure S1. XPS spectra of C 1*s* core levels for HOPG (black) and Ta@Si_{16}/HOPG (red).

S2. XPS measurements for O 1*s* core level

Figure S2 shows XPS spectra measured around O 1*s* core level for Ta@Si_{16} deposited on the C_{60} film before and after heat treatment. No O 1*s* signal was detected in the as-deposited sample (300 K). After thermal treatment at 520 K, O 1*s* signal appeared, indicating that heating shifted the Si 2*p* peak toward higher binding energy for Ta@Si_{16} (see Fig. 3a, main text). This indicates that Si atoms of Ta@Si_{16} were partially oxidized. Oxygen atoms may originate from the layered structure of HOPG upon heating. The O 1*s* peak intensity increased upon further heating, probably because the residual oxygen gradually oxidized the $(Ta@Si_{16})^{+}C_{60}^{-}$ during heating.

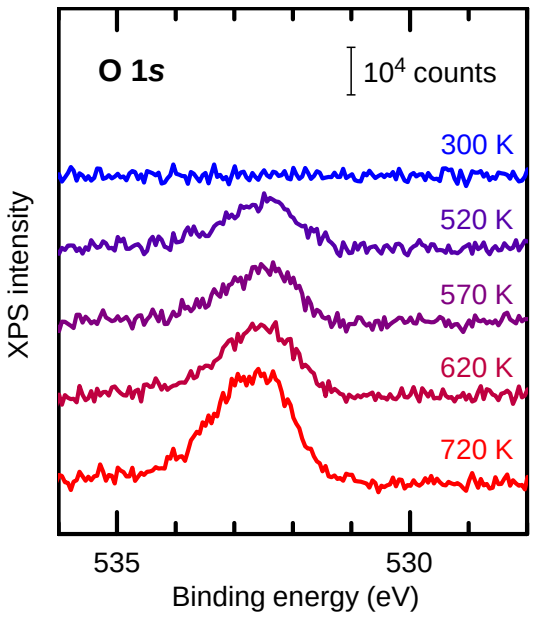

Figure S2. XPS spectra of O 1*s* core levels for Ta@Si_{16}/C_{60}/HOPG before and after heating. The heating temperatures are shown in the spectra.

S3. UPS and C 1*s* XPS analysis for heated samples

Figure S3(a) shows UPS spectra for Ta@Si_{16}/C_{60}/HOPG before and after heating. Because secondary electrons exhibited an exponentional behavior, backgrounds (gray dashed lines) were fitted assuming that no electronic structures existed in 5.0–4.5 and 0.5–0.0 eV regions. Based on this assumption, the peak areas (diagonal stripes) were evaluated and plotted against heating temperature in Fig. S3(b). The relative area represents the relative amount of residual C_{60} on the HOPG substrate.

Based on the residual C_{60} estimate, the C 1*s* XPS spectra could be deconvoluted for Ta@Si_{16}/C_{60}/HOPG before and after heating (Fig. S4). The spectrum at 300 K (Fig. 1(c), top) was deconvoluted into three components: the HOPG (G), the free C_{60} fullerenes (F), and the Ta@Si_{16}-C_{60} complexes (T). It seemed reasonable to assume that free C_{60} fullerenes (F) were desorbed upon heating at 520 K, which enabled further deconvolution of the XPS spectra into components G and T. For the C 1*s* spectrum at 520 K, when (1) the area of T was conserved and (2) the peak position of G maintained the same, the peak was deconvoluted into T′ and G components (Fig. S4). The component T′ slightly shifted to higher binding energy compared to T, probably because the heat treatments would deform the bilayer structure of the uppermost Ta@Si_{16} and adjacent C_{60} layers. Moreover, some C_{60} molecules may share an electron with another C_{60} by reconstructing the CT complex to others, such as a C_{60}-Ta@Si_{16}-C_{60}.

Above 520 K, component G further increased when the area T′ was assumed to decrease with the estimated C_{60} densities (Fig. S3(b)). The deconvolution result showed that the decoration layers on HOPG became thinner with increasing heating and bare HOPG surfaces largely appeared by the deformation of layered structures. In fact, multiply layered islands were formed (Fig. S5).

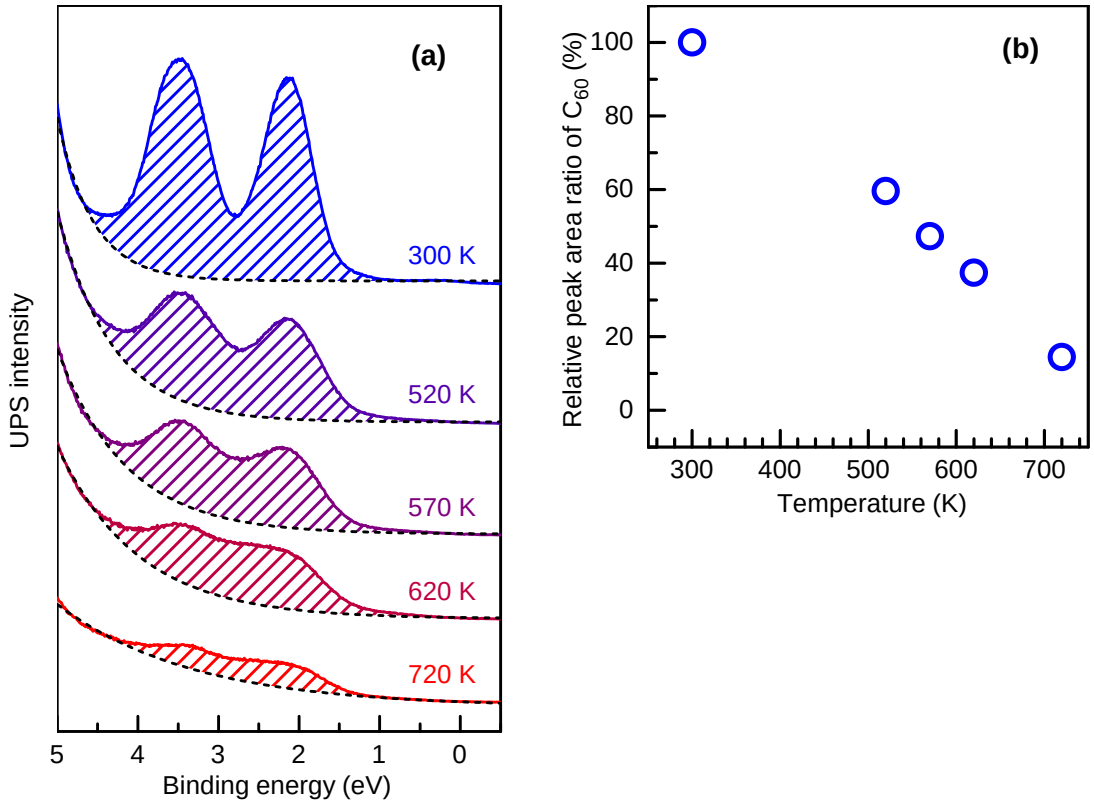

Figure S3. (a) UPS spectra for Ta@Si_{16}/C_{60}/HOPG measured before and after heating. The heating temperatures are noted in the right side. Backgrounds formed by secondary electrons are shown as gray dashed lines. The UPS signals areas of C_{60} are shown as diagonal stripes. They are plotted against temperatures in (b), where the areas are normalized with that at 300 K.

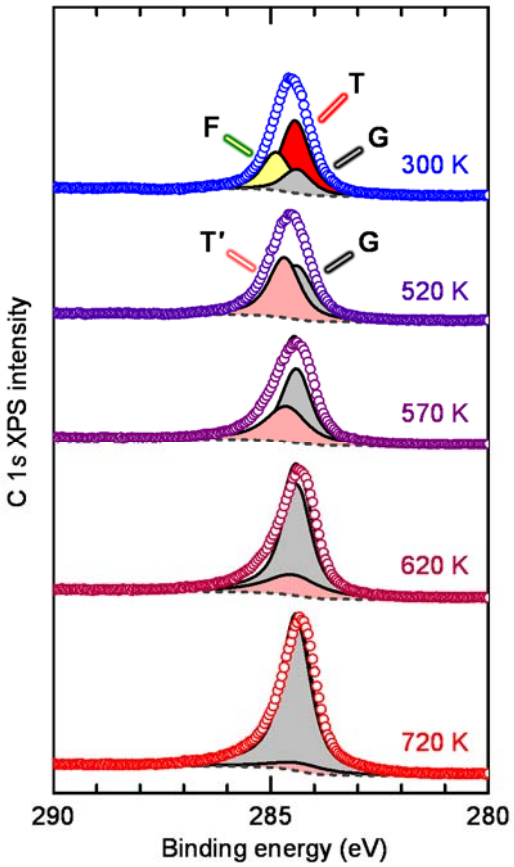

Figure S4. C 1*s* XPS spectra of Ta@Si_{16}/C_{60}/HOPG in each temperature. The circles show the original XPS data, and the heating temperature is overwritten in the right hand. The spectrum of Ta@Si_{16}/C_{60}/HOPG at 300 K was deconvoluted into three peaks: T (red), F (yellow), and G (gray). The other spectra were deconvoluted into two peaks: T′ (pink) and G peaks (gray) by assuming that T at 300 K equals to T′ at 520 K. Above 520 K, T′ at 520 K lessens with the decrease in the UPS intensities for C_{60} (Fig. S3b).

S4. STM image of Ta@Si_{16}/C_{60}/HOPG after heating at 720 K

Figure S5(a) shows an STM image (100 × 100 nm^2) of Ta@Si_{16}/C_{60}/HOPG after heating at 720 K for 16 h. Island structures consisting of small dots with a height of 2–3 nm are formed on a flat HOPG surface. This result indicates that free C_{60} molecules were desorbed from HOPG during heating. Figure S5(b) shows a magnified image (50 × 50 nm^2)

for the dense region where $Ta@Si_{16}$ nanoclusters cover the substrate. Even after the thermal treatment at 720 K, dot structures were distinguishable in the image, suggesting the robustness of the $Ta@Si_{16}$ caged framework.

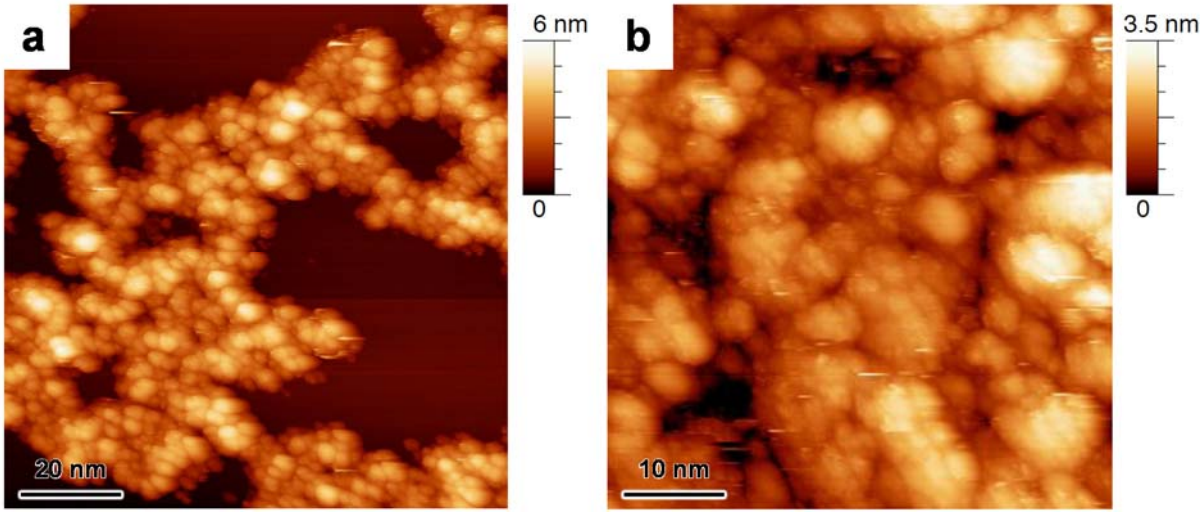

Figure S5. STM images of $Ta@Si_{16}/C_{60}$/HOPG after heating at 720 K of (a) (100 × 100 nm^2) and (b) magnified for islands (50 × 50 nm^2).