Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION FOR

Dependence of Hot Electron Transfer on Surface Coverage and Adsorbate Species at Semiconductor-Molecule Interfaces

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S1. Interface Models

The H-Si(111) surface was modeled using a 3×3 supercell with eight layers of 144-Si-atom surface slab (with a surface area of ~0.45 nm^2 and thickness of ~2.4 nm) in this work. The bottom three layers were held fixed in the bulk positions during the FPMD simulations. The slab was separated from its periodic images along the surface normal by a vacuum region of 15 Å such that the interaction between the repeating slabs is negligible. Side view of the four interface models investigated in this work is shown in Figure S1.

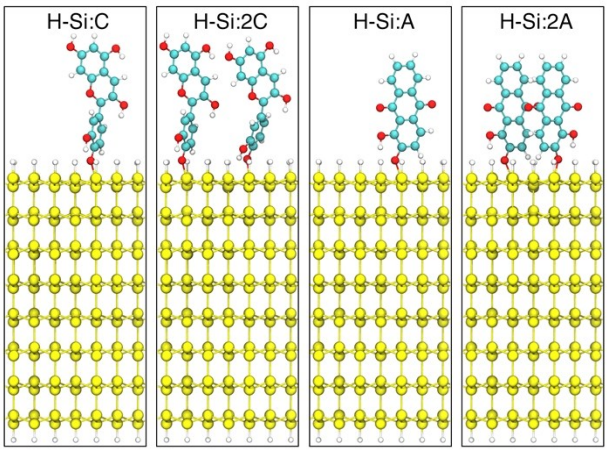

Figure S1. Side view of the interface models investigated in this work.

The spatial-resolved density of states (DOS) of the unoccupied electronic states for the interfaces of **H-Si:C** and **H-Si:2C**, **H-Si:A**, and **H-Si:2A** are shown in Figure S2, where the surface conduction band minimum (CBM) is set as the reference energy of 0. The spatial-resolved DOS is calculated by averaging the electron density in the surface plane. As can be seen in Figure S2, the unoccupied electronic states of the Alizarin molecule are energetically situated above the surface CBM, so that fast and efficient interfacial electron transfer could take place,[1] making it another ideal interface model to investigate HET process.

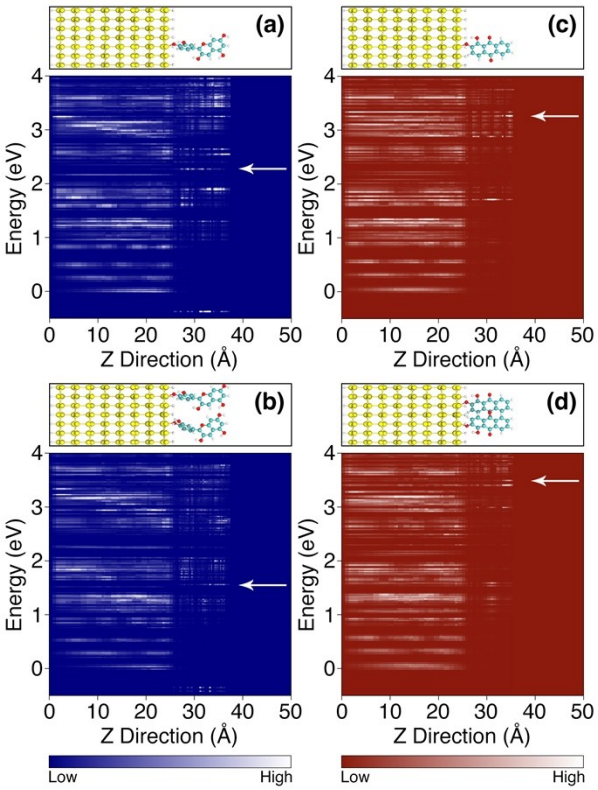

Figure S2. Spatial-resolved density of states for (a) **H-Si:C**, (b) **H-Si:2C**, (c) **H-Si:A**, and (d) **H-Si:2A** interfaces, where the DOS is calculated by averaging the electron density in the surface plane. Hot electron states are indicated by arrows and the surface CBM is set as the reference energy of 0 eV in the spatial-resolved DOS figures.

S2. Peak Probability of Excited Electron within Unoccupied Electronic States and the Hot Electron Accepting Molecular States

Peak probability of the excited electron within the unoccupied electronic states as a function of state index based on time-averaged energy is shown in Figure S3, together with the wave function contribution from the adsorbate for each unoccupied electronic state. The red color indicates that the wave function is mainly localized on the surface adsorbate. Here, we consider an electronic state as a pure molecular state only if its wave function has more than 80% contribution from the adsorbed molecule. Among all the pure molecular states depicted by red color, the one with the largest hot electron probability is labeled by triangle marker, and is referred to as hot electron state throughout this work. Although the high surface coverage interfaces (**H-Si:2C** and **H-Si:2A**) provide more molecular states localized on the adsorbed molecule (red dots in Figure S3) than the low coverage interfaces (**H-Si:C** and **H-Si:A**), the hot electron state becomes highly delocalized on both adsorbed molecules as can be seen in Figure 3b in the main text. Except for the hot electron states labeled in Figure S3, there are no other molecular states that exhibit significant hot electron probability although there exist other molecular states with lower energies as shown in Figure S3. In other words, there is no excited electron relaxation within the molecule after the excited electron transfers into the molecule from the semiconductor. Rather, the hot electron quickly transfers back to the semiconductor before it has time to relax within the molecule.

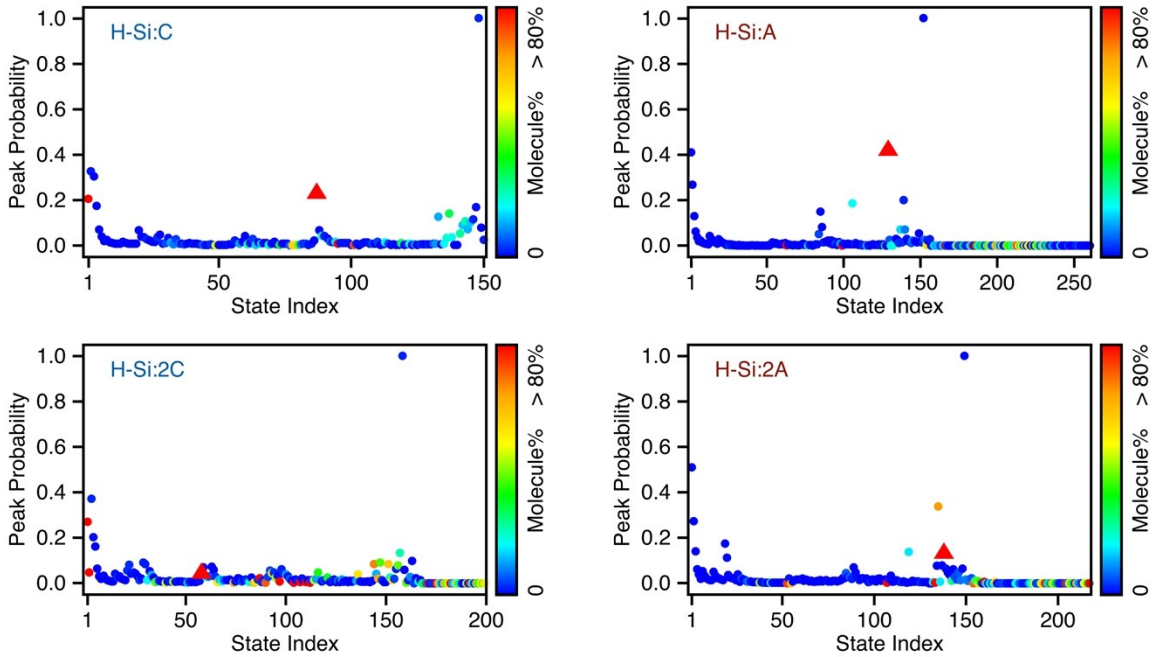

Figure S3. Peak probability of the hot electron within the unoccupied electronic states as a function of state index based on time-averaged energy, together with the wave function contribution from the adsorbate molecule for each unoccupied electronic state. Red triangle marker represents the pure molecular state with the largest hot electron probability and is referred to as hot electron state.

S3. Surface-induced Delocalization of the Hot Electron States for Cyanidin

Isosurface of the molecular states that correspond to the hot electron state of the **H-Si:C** interface for the two Cyanidin molecules are shown in Figure S4a. The geometry of two Cyanidin molecules are directly taken from the **H-Si:C** interface as shown in Figure S1, and the bottom two oxygen atoms are terminated by hydrogen atoms (instead of the silicon surface). As can be seen in Figure S4a, the molecular states for the two molecules without the surface are highly localized on individual molecules although there are no such corresponding states at the **H-Si:2C** interface (see the main text for discussion). When the H-Si(111) surface was placed close to the two Cyanidin molecules with a separation distance of 1 angstrom as shown in Figure S4b, the molecular states become highly delocalized on both molecules as in the case of the **H-Si:2C** interface. The reason why the hot electron state does not remain localized on individual molecules is not because of the inter-molecular interaction but because of the presence of the semiconductor surface with significant "spilling" of the electron density into the vacuum region away from the surface.

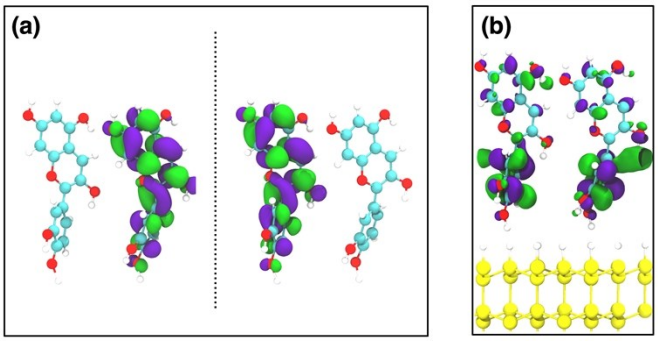

Figure S4. Isosurface of the single-particle Kohn-Sham electronic wave function of the molecular states for (a) isolated two Cyanidin molecules, (b) the interface between Cyanidin molecules and the H-Si(111) surface with a separation distance of 1 angstrom. The geometry of the Cyanidin molecules was taken directly from the **H-Si:C** interface, where the bottom two oxygen atoms were terminated by hydrogen atoms.

S4. Nonadiabatic Couplings

Time-averaged magnitudes of the nonadiabatic coupling (NAC) matrix for the unoccupied electronic states at the four interfaces are shown in Figure S5, where the position of the hot electron state is labeled out in the matrix by arrows. The NACs between hot electron state and other semiconductor states are shown in Figure S6.

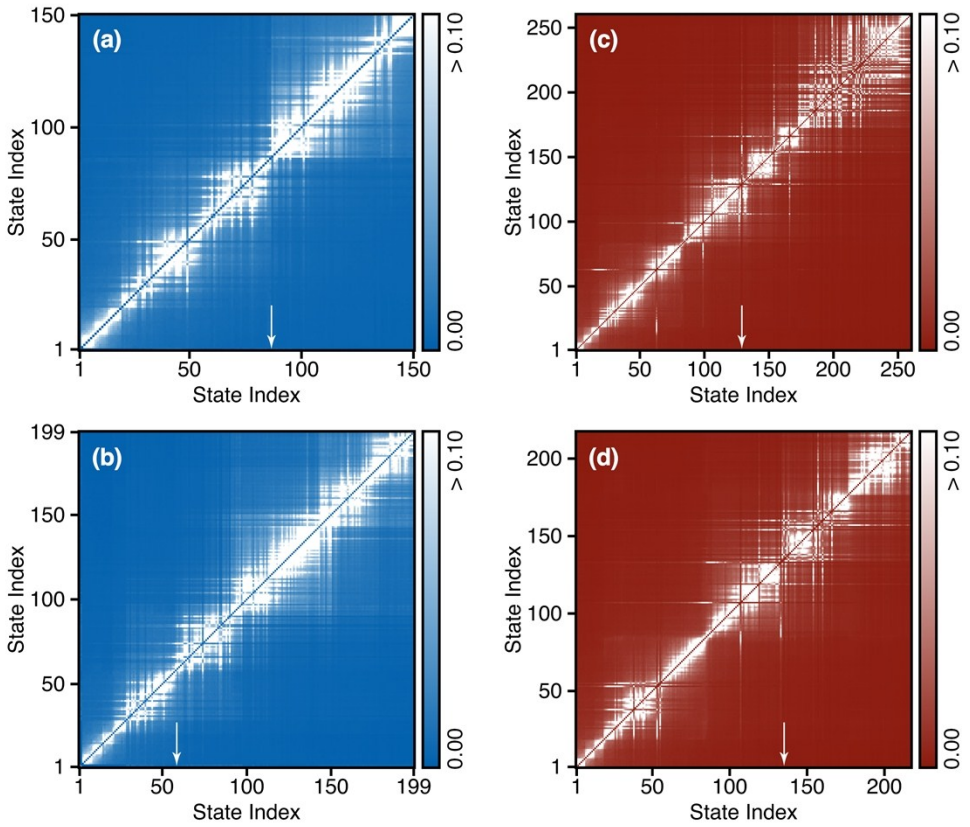

Figure S5. Nonadiabatic coupling (NAC, in a.u.) matrices for the unoccupied electronic states at the four interfaces of (a) **H-Si:C**, (b) **H-Si:2C**, (c) **H-Si:A**, and (d) **H-Si:2A**. The position of the hot electron state is labeled out in the matrix by arrow.

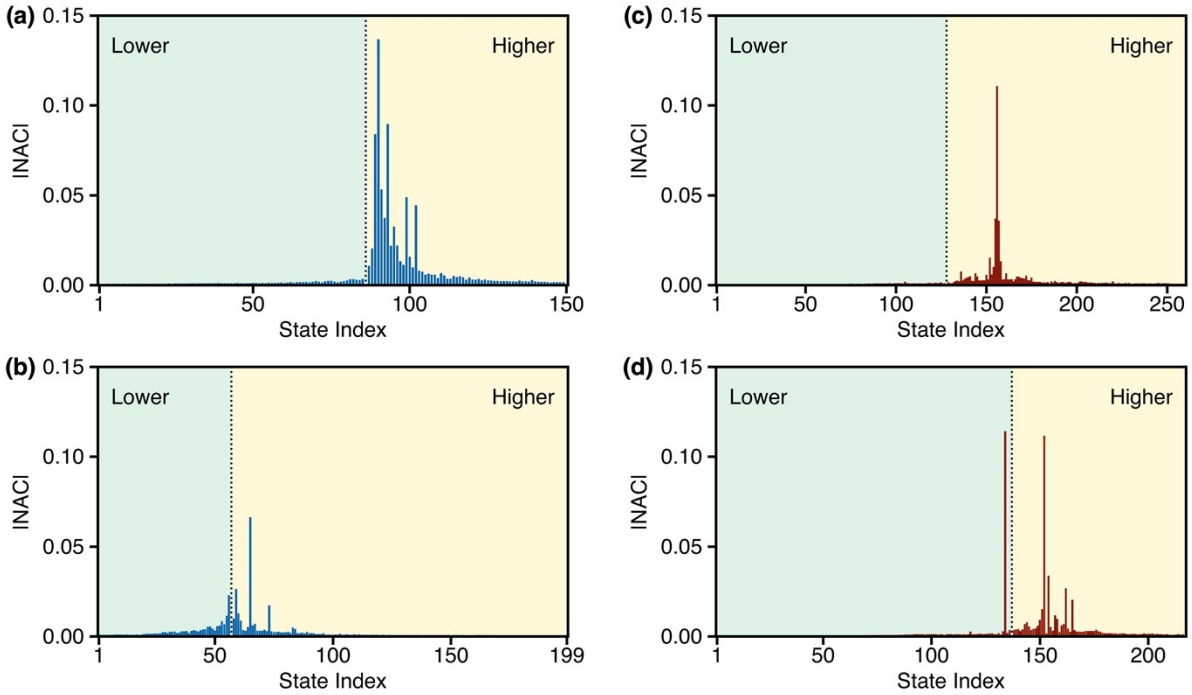

Figure S6. NACs (in a.u.) between the hot electron state and the unoccupied semiconductor states at the four interfaces of (a) **H-Si:C**, (b) **H-Si:2C**, (c) **H-Si:A**, and (d) **H-Si:2A**. The positions of the hot electron states are labeled out in the matrix by dash lines.

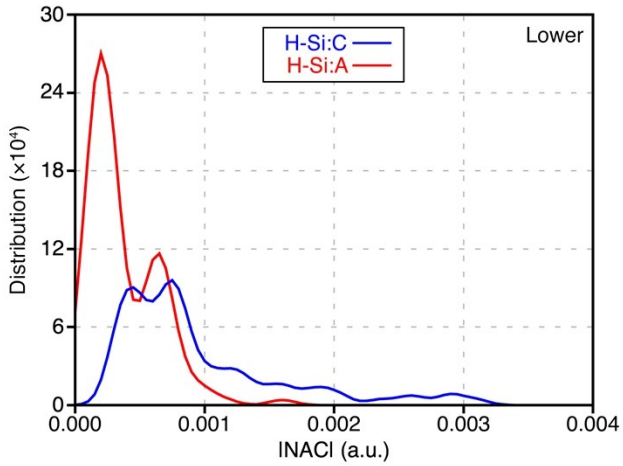

Figure S7. Distribution of NAC magnitude between the hot electron state and the lower-lying semiconductor states at the **H-Si:C** (blue) and **H-Si:A** (red) interfaces. Bin size of 5×10^{-4} was used for the Gaussian broadening where $\sigma^2=5\times10^{-7}$.

S5. Probability Change for Hot Electron State Before and After Shifting Energy Level

In order to examine if the significant HET probability for the **H-Si:A** interface could be also due to the fact that the hot electron state is energetically close to the initial excited state in the semiconductor, we performed another simulation for the **H-Si:A** interface with the hot electron state that is artificially shifted away to be the same energy as the **H-Si:C** case. The comparison of the probability change for the hot electron state before and after shifting the hot electron state at the **H-Si:A** interface as well as the one at the **H-Si:C** interface is shown in Figure S8. As can be seen in Figure S8, the artificially-constructed simulation yields even higher HET probability compared to the original case, indicating that the energetic proximity of the hot electron state to the initial excited state is not the reason for the significant higher HET probability at the **H-Si:A** interface compared to the **H-Si:C** case as shown in Figure 3a. What we found in comparison between **H-Si:A** and **H-Si:A^{shift}** is that the excited electron in the semiconductor transition to other semiconductor states more predominantly when the hot electron state is high-lying (the **H-Si:A** case). When the hot electron state is lower in energy, the excited electron is transitioned from more number of semiconductor states into the hot electron state while the hot electron undergoes relaxation within the semiconductor.

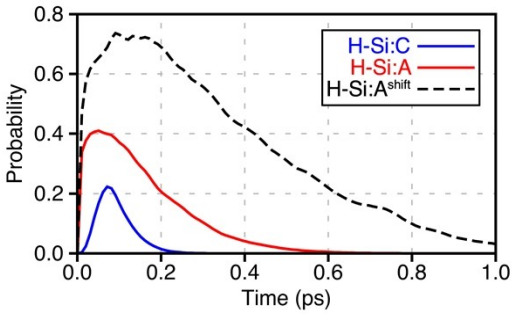

Figure S8. Probability change of the hot electron state for the interfaces of **H-Si:C** (blue), **H-Si:A** (red), and **H-Si:A^{shift}** (dashed black). **H-Si:A^{shift}** represents the case where the hot electron state was artificially shifted away to the same energy of the **H-Si:C** interface.

S6. Ensemble Averaged Energy for Excited Electron

In order to show the deviation from the exponential decay for the averaged energy for the excited electron as shown in Figure 2 of the main text, we plot the ensemble averaged energy for the excited electron with log-scale for the energy axis in Figure S9. We need to point out here that since the lowest unoccupied electronic state for the attached molecule at the **H-Si:C** and **H-Si:2C** interfaces are located energetically lower than the surface CBM (-0.37 eV for **H-Si:C** and -0.42 eV for **H-Si:2C**), we shifted the ensemble averaged energy upward by 0.37 eV and 0.42 eV for the **H-Si:C** and **H-Si:2C** interfaces, so we could plot in the log-scale for the energy axis. Meanwhile, the ensemble averaged energy for the **H-Si:A** and **H-Si:2A** interfaces remains the same.

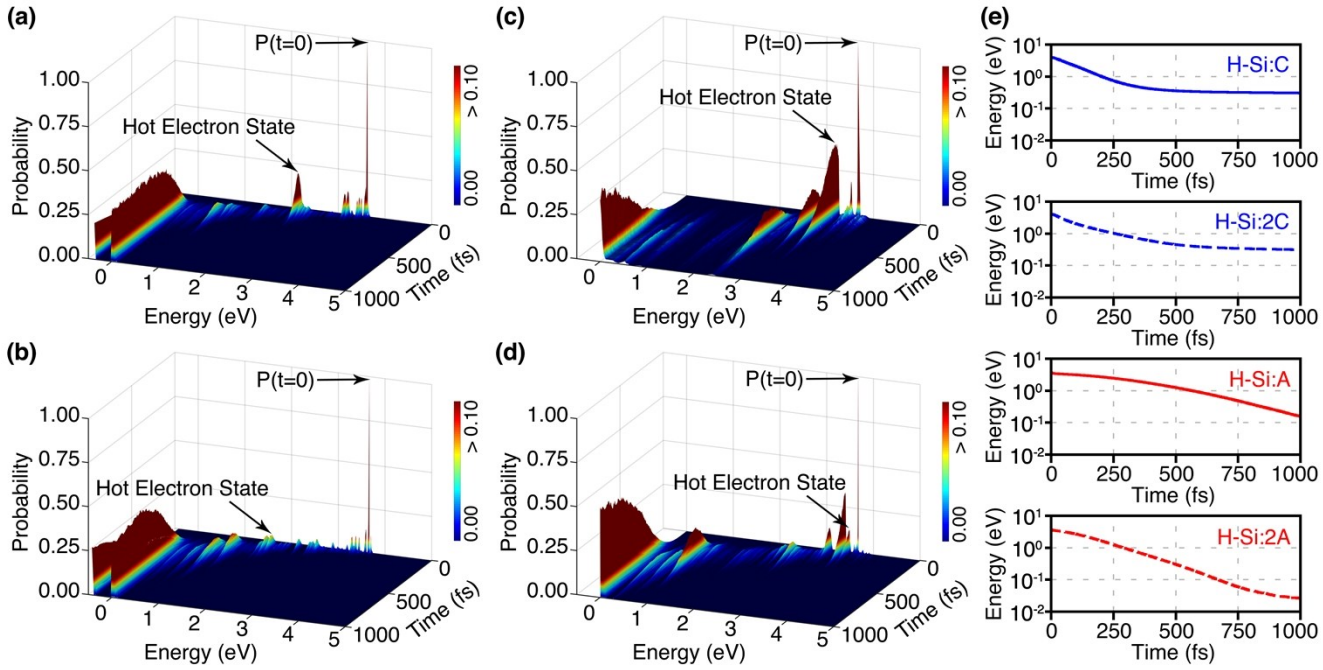

Figure S9. Probability of locating the excited electron at a specific energy as a function of time at the interfaces of (a) **H-Si:C**, (b) **H-Si:2C**, (c) **H-Si:A**, and (d) **H-Si:2A**, together with the (e) ensemble averaged energy for the excited electron. The energy axis is given by log-scale in (e). The reference energy of 0 eV corresponds to the surface CBM. The hot electron accepting state that dominantly localized on the molecule is referred to as hot electron state. The excited electron was initially populated in a semiconductor state with energy of ~3.6 eV above the surface CBM and is indicated by P(t=0).

S7. Coordinates of the Interface Models

H-Si:A:

H 7.680197236 2.216856524 0.000026292
H 0.000413923 2.216871081 0.000032486
H 3.840293733 8.867714437 0.000036114
H 3.840056694 2.216863538 0.000038398
H 1.920277040 5.542840144 0.000037492
H 0.000240451 8.867825259 0.000037019
H -1.919705837 5.542897280 0.000039258
H 5.760131684 5.543007190 0.000044104
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Si 0.000000000 2.217000000 1.501180000
Si -0.000000000 8.868000000 1.501180000
Si 1.920000000 5.543000000 1.501180000
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Si 3.840000000 8.868000000 8.556180000
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C 6.806256761 2.660798442 29.596844251
O 3.666011288 4.397339098 30.667890012
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C 7.215012073 2.422345163 33.414333690
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H-Si:2A

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Si 5.760000000 3.326000000 7.772180000
Si 7.680000000 0.000000000 7.772180000
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Si -3.840000000 6.651000000 7.772180000
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C 3.429454055 3.537384139 28.251785989
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C 5.412498870 2.700148593 29.475042322
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H-Si:C

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H-Si:2C

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