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

Supporting Information

Probing the electronic structure and Au–C bonding in $AuC_{2n}H$ (n = 4-7) using photoelectron imaging spectroscopy and quantum chemical calculations

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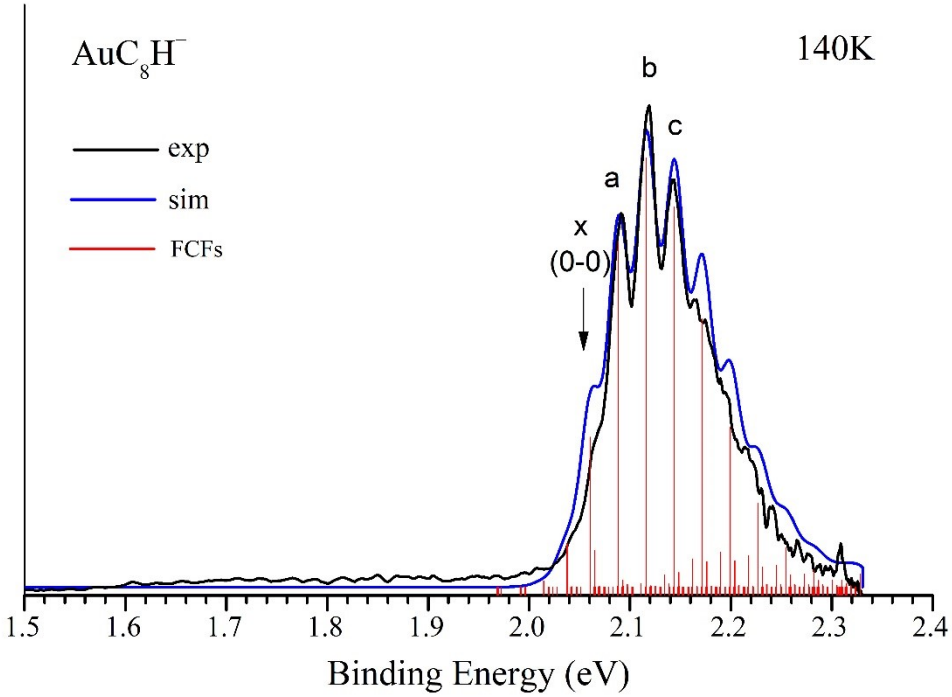

Fig.S1 The PE spectrum (black) at 532 nm, FC simulated curve (blue), and calculated FC factors (red stick) for Au-C stretching vibrational transition, using CAM-B3LYP geometries, frequencies, and of ground anionic and neutral AuC_8H are shown to make comparison. The assignment of 0-0 transition peak at 2.063 eV is given.

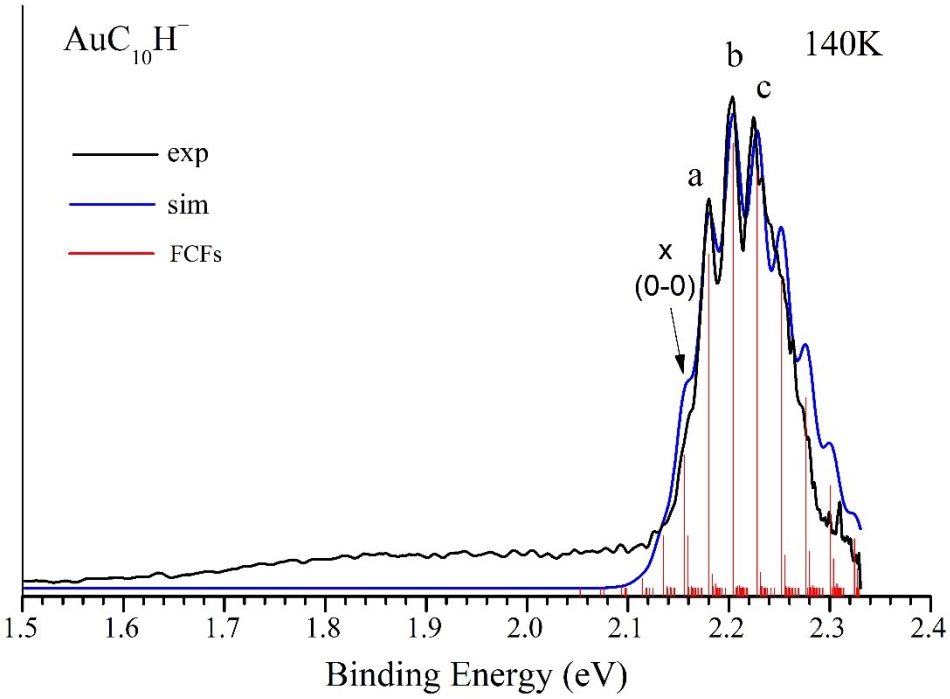

Fig.S2 The PE spectrum (black) at 532 nm, FC simulated curve (blue), and calculated FC factors (red stick) for Au-C stretching vibrational transition, using CAM-B3LYP geometries, frequencies, and of ground anionic and neutral $AuC_{10}H$ are shown to make comparison. The assignment of 0-0 transition peak at 2.157 eV is given.

Since electronic bonding energy is close to the detachment photo energy, the PE spectra for $AuC_{12}H^-$ and $AuC_{14}H^-$ are incomplete and difficult to give the FC simulation. For $AuC_{12}H^-$ and $AuC_{14}H^-$, the 0-0 transition (labeled as *x*) are extrapolated to the position at the lower energy of peak *a* by one vibrational quantum of Au-C stretching mode in the neutral ground state.

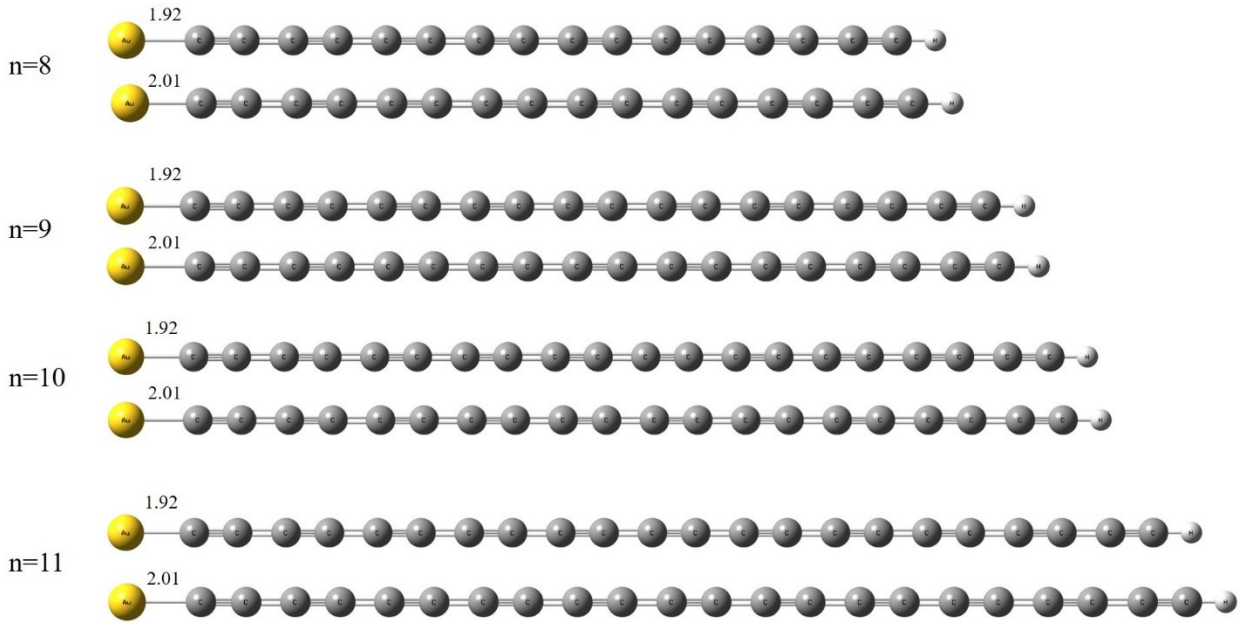

Fig.S3 Optimized molecule structures of $AuC_{2n}H^-$ (n = 8-11) and their corresponding neutrals at the CAM-B3LYP/AVTZ level. For each n, the bottom shows the anion structure, while the top structure is for the neutral. All bond lengths are shown in Å.

Table S1. The theoretical ADEs of $AuC_{2n}H^-$ (n = 8-11) at CAM-B3LYP/AVTZ level.

Number of n	CAM-B3LYP (eV)
8	2.301
9	2.325
10	2.346
11	2.357