Electronic Supplementary Information (ESI)

Polymorphism of $Au_{11}(PR_3)_7Cl_3$ clusters: Understanding C-H···π interaction and C-H···Cl-C van der Waals interaction on cluster assembly by surface modification

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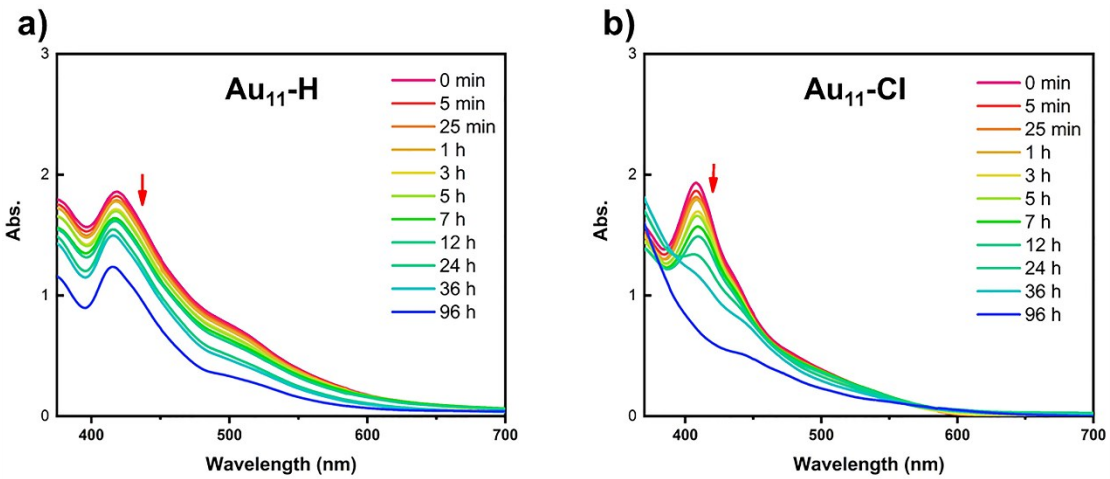

Figure S1. UV-vis spectra confirming the thermal stability of **Au_{11}-H** (a), **Au_{11}-Cl** (b) over time.

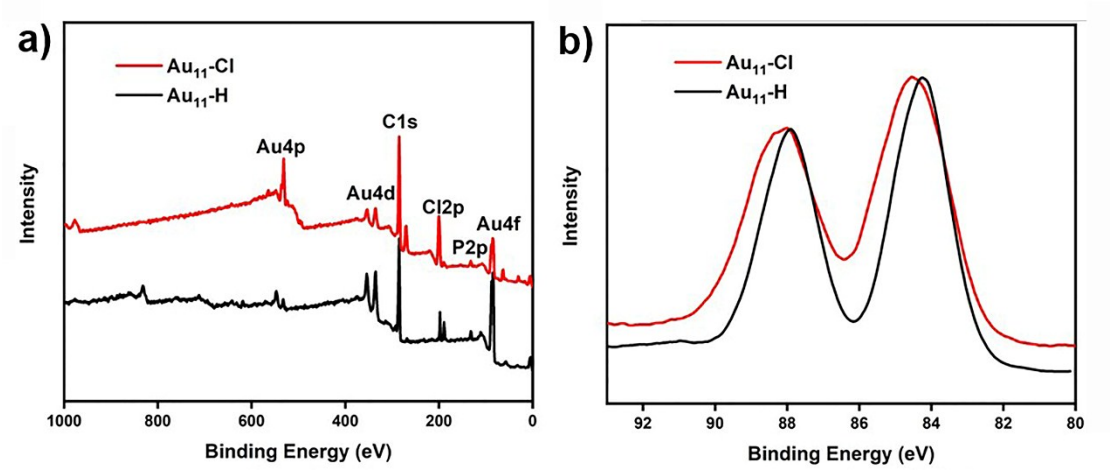

Figure S2. a) X-ray photoelectron spectra of **Au_{11}-Cl** and **Au_{11}-H**; b) XPS of Au4f in the **Au_{11}-Cl** and **Au_{11}-H**.

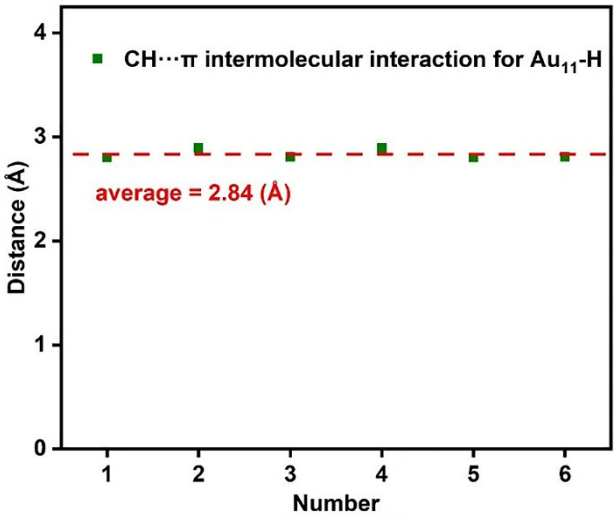

Figure S3. The statistical histogram of the CH···π interactions for **Au_{11}-H**.

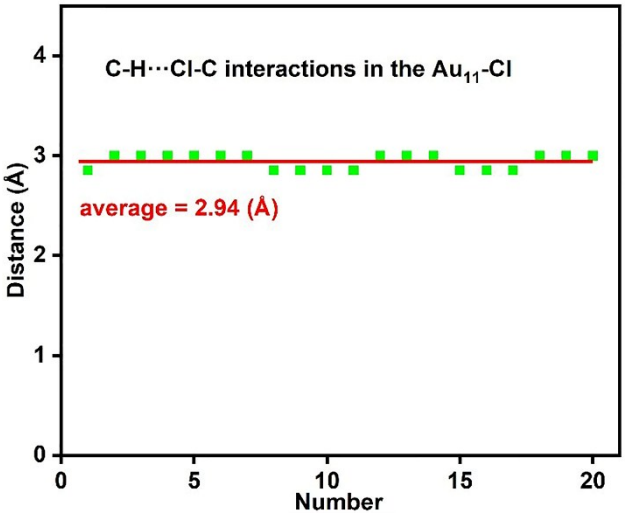

Figure S4. The statistical histogram of C-H···Cl-C interactions for **Au_{11}-Cl**.

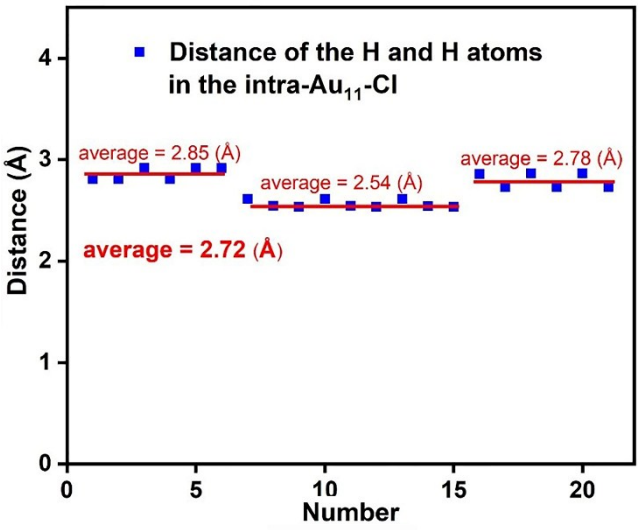

Figure S5. The statistical histogram of the intra-D_{HH} in the **Au_{11}-Cl**.

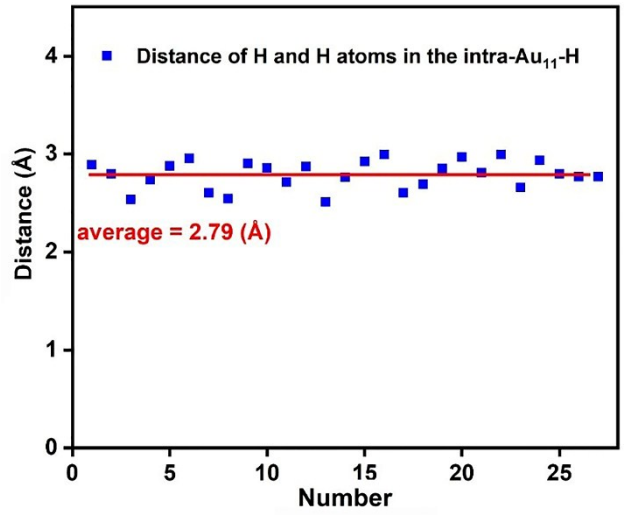

Figure S6. The statistical histogram of the intra-D_{HH} in the **Au_{11}-H**.

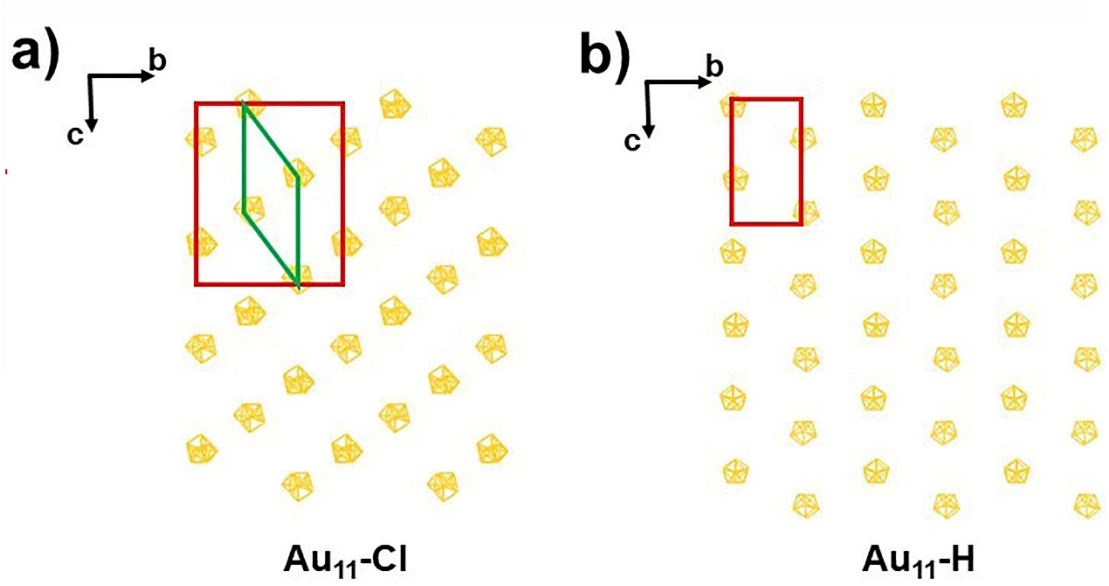

Figure S7. The superlattice of the **Au_{11}-Cl** (**T**) and **Au_{11}-H** (**M**) view from the a-axis.

Table S1. Crystal data and structure refinement for the **Au_{11}-Cl** and **Au_{11}-H**[a].

Identification code	$Au_{11}(PPh_3)_7Cl_3$	$Au_{11}(p\text{-}ClPPh_3)_7Cl_3$
Empirical formula	$C_{129}H_{112}Au_{11}Cl_4\ P_7$	$C_{126}H_{84}Au_{11}Cl_{24}P_7$
Formula weight	4187.41 g mol^{-1}	4832.200 g mol^{-1}
Crystal system	Monoclinic	Trigonal
Space group	P2(1)/n	R-3
Length a	17.864(3) Å	27.949(4) Å
Length b	25.801(5) Å	27.949(4) Å
Length c	26.912(5) Å	34.439(5) Å
Angle alpha	90.00°	90.000°
Angle beta	91.809(3)°	90.000°
Angle gamma	90.00°	120.000°
volume	12398(4) $Å^3$	23297.7(80) $Å^3$
Formula units Z	4	6
Density	2.243	2.066

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References:

1. L. C. McKenzie, T. O. Zaikova and J. E. Hutchison, *J Am Chem Soc*, 2014, **136**, 13426-13435.