C-H···Au interaction and optical properties in $[(P,P)_4Au_6]^{2+}$ molecular gold nanoclusters.

Laura Estévez

Departamento de Química Física, Universidade de Vigo, As Lagoas-Marcosende s/n, 36310 Galicia, Spain
lestevez@uvigo.es.

Supplementary Material

Table S1. Main geometrical features (in Å and º) of the [core+exo] Au_6 units together with PP distance and PAuP bond angle of the main systems studied here.

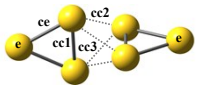	*cc1*	*cc2*	*cc3*	*ce*	*ee*	d(PP)	PAu_eP
1	2.689	2.964	2.989	2.885	7.394	5.527	137.5
1 (gas phase)	2.687	2.957	3.010	2.880	7.396	5.535	137.4
$\mathbf{1_{Me\text{-}op}}$	2.665	2.964	3.029	2.882	7.441	5.511	142.7
$\mathbf{1_{H\text{-}op}}$	2.647	2.994	3.063	2.872	7.479	5.490	144.2
2	2.669	2.987	3.043	2.901	7.502	5.550	139.7
2 (gas phase)	2.670	2.948	3.064	2.889	7.461	5.555	138.0
$\mathbf{2_{Me\text{-}op}}$	2.655	2.981	3.011	2.893	7.475	5.519	143.0
$\mathbf{2_{H\text{-}op}}$	2.643	3.001	3.002	2.873	7.450	5.456	143.8
$\mathbf{[Au_6]^{2+}}$	2.722	2.876	2.876	2.680	6.754	---	---
$\mathbf{[Au_6]^{2+}}$ **(gas phase)**	2.690	2.942	2.944	2.703	6.933	---	---

Table S2. Main geometry features of the C-H···Au interaction in optimized geometries of **1** and **2** in CH_2Cl_2 and in the gas phase.

Cluster	**Distances (Å)**				**Angle (º)**
	C-H	H···Au	BPL	$\Delta_{BPL-d(H\cdots Au)}$	CHAu
1 (gas phase)	1.088	2.636	2.675	0.039	174.8
1	1.088	2.630	2.669	0.038	175.2
2 (gas phase)	1.098	2.829	2.948	0.119	173.0
2	1.098	2.777	2.828	0.051	175.3

BPL: Bond path length.

Table S3. ^{1}H NMR chemical shifts (reference to TMS).

	1	mPhDP	$\mathbf{1_H}$	$\mathbf{1_{H\text{-}op}}$
H2	12.07	8.37	11.04	10.73
H4, H6	7.52, 7.27	7.36, 7.19	8.22, 7.98	8.18, 7.92
H5	7.70	7.51	7.75	7.70
	2	TMDP	$\mathbf{2_H}$	$\mathbf{2_{H\text{-}op}}$
H2	4.47	1.55	3.87	3.82
H1, H3	2.53	2.49	1.84	1.89
H2’	1.51	1.50	1.36	1.41

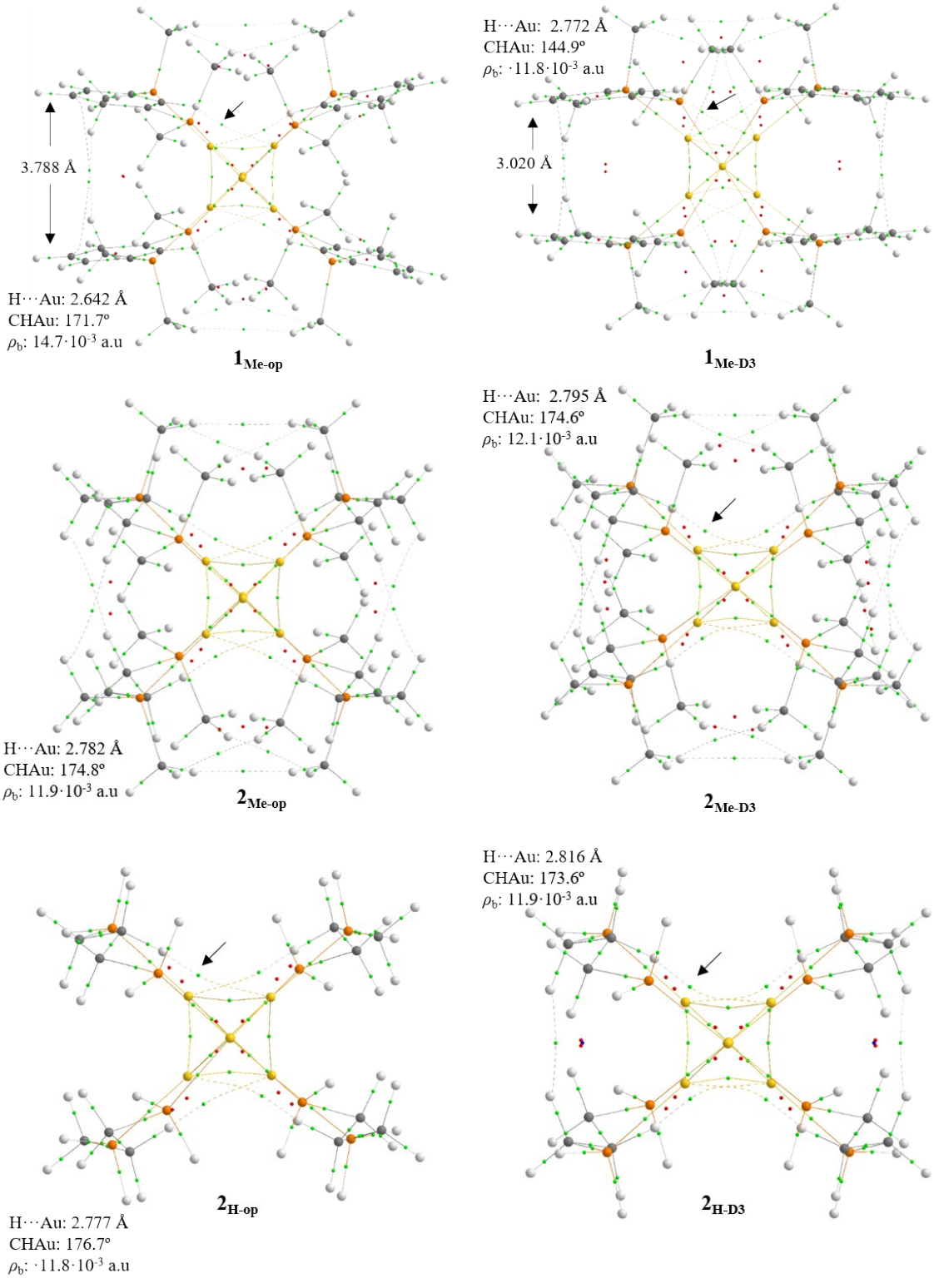

Figure S1. QTAIM plots of $\mathbf{1}_{Me}$, , $\mathbf{1}_{Me\text{-}D3}$, $\mathbf{2}_{Me}$, $\mathbf{2}_{Me\text{-}D3}$, $\mathbf{2}_{H}$ and $\mathbf{2}_{H\text{-}D3}$. **An arrow is shown to localte one of the four equivalent CH···Au BCP's.**

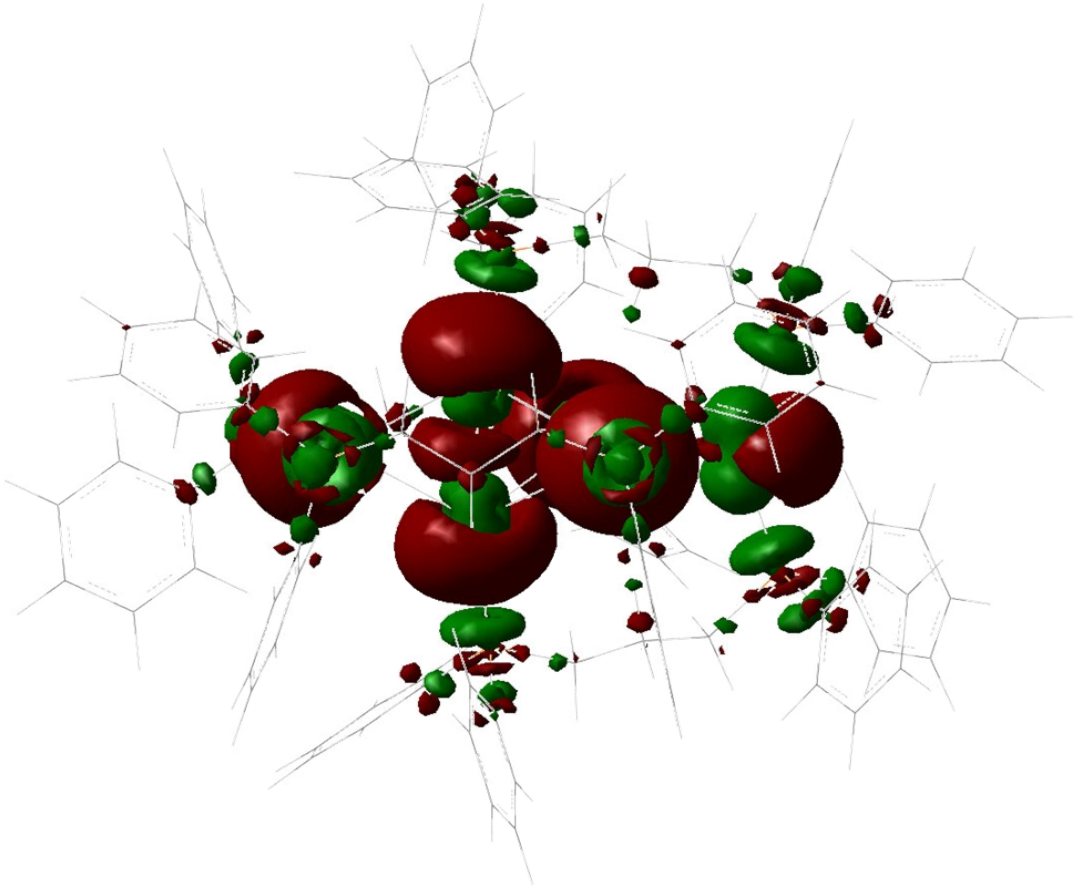

Figure S2. $\Delta\rho^{def}(r)$ of cluster **2** where red and green denote, respectively, enhancement and depletion of the electron density upon L-Au_6 binding (cutoff 0.0003 a.u.).