Supporting information for:

# On the Halide Aggregation into $[Au_4(PPh_3)_4]^{4+}$ Cluster Core. Insights from Structural, Optical and Interaction Energy Analysis in $[(Ph_3PAu)_4X_2]^{2+}$ and $[(Ph_3PAu)_4X]^{3+}$ species ($X=Cl^-$, $Br^-$, $I^-$)

Raul Guajardo-Maturana,[a] Peter. L. Rodríguez-Kessler,[b] and Alvaro Muñoz-Castro[c*]

[a]*Universidad SEK, Facultad de Ciencias de la Salud, Instituto de Investigación Interdisciplinar en Ciencias Biomédicas SEK (I3CBSEK) Chile, Fernando Manterola 0789, Providencia, Santiago, Chile*
[b]*Centro de Investigaciones en Óptica A.C., Loma del Bosque 115, Col. Lomas del Campestre, León, Guanajuato, 37150, Mexico.*
[c]*Facultad de Ingeniería, Arquitectura y Diseño, Universidad San Sebastián, Bellavista 7, Santiago, 8420524, Chile.*

Content

Table S1. HOMO-LUMO gap (eV) for the studied species at the TZ2P/PBE and TZ2P/PBE0 level of theory.

| | PBE | PBE0 |
|---|---|---|
| 1a | 3.05 | 4.786 |
| 2a | 3.033 | 4.619 |
| 3a | 3.089 | 4.719 |
| | | |
| 1b | 1.713 | 3.227 |
| 2b | 1.521 | 2.995 |
| 3b | 1.254 | 2.695 |

Table S2. Energy decomposition analysis for the $(Ph_3PAu)_4^{4+}$-$X^-$ interaction in mono- and dihalide species, given per halide, at the hybrid TZ2P/PBE0 level of theory. Values in kcal·mol$^{-1}$.

| | **1a** | | **2a** | | **3a** | |
|---|---|---|---|---|---|---|
| $\Delta E_{Pauli}$ | 193.2 | | 184.6 | | 200.9 | |
| $\Delta E_{elstat}$ | -354.6 | 77.4% | -341.3 | 76.9% | -349.4 | 76.5% |
| $\Delta E_{orb}$ | -97.3 | 21.2% | -94.6 | 21.3% | -97.1 | 21.2% |
| $\Delta E_{disp}$ | -6.5 | 1.4% | -7.9 | 1.8% | -10.4 | 2.3% |
| | | | | | | |
| $\Delta E_{int}$ | -265.1 | | -259.2 | | -255.9 | |
| | | | | | | |
| | **1b** | | **2b** | | **3b** | |
| $\Delta E_{Pauli}$ | 211.9 | | 190.1 | | 208.3 | |
| $\Delta E_{elstat}$ | -425.2 | 79.2% | -395.1 | 77.0% | -401.0 | 77.8% |
| $\Delta E_{orb}$ | -105.9 | 19.7% | -111.3 | 21.7% | -105.0 | 20.4% |
| $\Delta E_{disp}$ | -5.5 | 1.0% | -6.4 | 1.2% | -9.5 | 1.8% |
| | | | | | | |
| $\Delta E_{int}$ | -324.7 | | -322.7 | | -307.2 | |