

Supporting Information

Table S1. Structural, binding, charge-transfer and conceptual DFT parameters for all nine Au₁₀-L-DOPA complexes (zwitterionic, aqueous phase).

Isomer codes: PEH = planar elongated hexagon, CTP = capped trigonal prism, FF = folded flake.

| System | Isomer | d(Au-Au) _{avg} (Å) | d(Au-O) _{min} (Å) | ΔG _{bind} (kcal mol ⁻¹) | Δe ⁻ (e) ^a | ΔN ^b |
|----------------------------------|--------|--------------------------------|-------------------------------|---|-------------------------------------|-----------------|
| Au ₁₀ ⁺ -L | PEH | 2.748 | 2.188 | -31.8 | +0.529 | 0.927 |
| | CTP | 2.763 | 2.206 | -24.5 | +0.580 | 0.818 |
| | FF | 2.752 | 2.179 | -22.2 | +0.485 | 0.550 |
| Au ₁₀ ⁰ -L | PEH | 2.782 | 2.307 | -14.7 | +0.317 | 0.215 |
| | CTP | 2.769 | 2.312 | -22.9 | +0.315 | 0.215 |
| | FF | 2.749 | 2.186 | -17.3 | +0.244 | 0.215 |
| Au ₁₀ ⁻ -L | PEH | 2.771 | 2.364 | -9.8 | +0.223 | 0.296 |
| | CTP | 2.790 | 2.235 | -2.6 | +0.233 | 0.309 |
| | FF | 2.770 | 2.207 | -8.6 | +0.073 | 0.322 |

^a Hirshfeld charge transfer; positive values indicate net ligand-to-metal electron transfer.

^b Conceptual DFT charge transfer (ΔN) based on isolated fragment properties; positive values indicate donor→acceptor flow. For cations and neutrals the flow is L→Au; for anions it is Au→L.

All values correspond to fully optimized geometries at the B3LYP-D3/def2-TZVP level with SMD water. Binding free energies are reported to one decimal place; bond lengths and Δe⁻ are given to three decimal places as originally calculated.

Figure S1. Optimised structures of all nine Au_{10} -L-DOPA complexes (zwitterionic, aqueous phase).

The figure is arranged as a 3×3 grid: rows correspond to charge states (+1, 0, -1 from top to bottom), columns correspond to isomer types (PEH, CTP, FF from left to right). Colour code: Au (gold), O (red), N (blue), C (grey), H (white). All structures were optimised at the B3LYP-D3/def2-TZVP level with SMD water.

