[2.2.2]Paracyclophane, Preference for \( \eta^6 \) or \( \eta^{18} \) Coordination Mode Including Ag(I) and Sn(II): A Survey into the Cation-\( \pi \) Interaction Nature Through Relativistic Density Functional Theory Calculations.

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Supporting Information
**Figure S1.** Optimized structure for $[1$-Sn$]^{2+}$ and $[1$-Sn$]^{2+}$[AlCl$_4$]$^{-1}$.  

**Figure S2.** $\pi$-based levels of [2.2.2]paracycophane related to benzene for simplicity.
Figure S3. Molecular structure of the studied systems.
Figure S4 Contours of deformation densities, $\Delta \rho_i(r)$, describing the interaction between Ag$^+$ and [2.2.2]Paracyclophane, 1, and the corresponding energy, $\Delta E_{\text{orb}}^i$ (kcal.mol$^{-1}$), and charge estimation, $\Delta q_i$ (a.u.). Red and blue surfaces indicate density outflow and density inflow, respectively (contour value 0.0003).
Δρ₁, ΔE_{orb} = -38.9, Δq₁ = 0.588
Δρ₂, ΔE_{orb} = -38.9, Δq₂ = 0.516
Δρ₃, ΔE_{orb} = -38.9, Δq₃ = 0.516
Δρ₄, ΔE_{orb} = -8.3, Δq₄ = 0.157
Δρ₅, ΔE_{orb} = -8.2, Δq₅ = 0.156
Δρ₆, ΔE_{orb} = -7.9, Δq₆ = 0.155
Δρ₇, ΔE_{orb} = -7.9, Δq₇ = 0.155
Δρ₈, ΔE_{orb} = -5.5, Δq₈ = 0.114
Δρ₉, ΔE_{orb} = -3.0, Δq₉ = 0.084
Δρ₁₀, ΔE_{orb} = -2.8, Δq₁₀ = 0.094
Δρ₁₁, ΔE_{orb} = -2.0, Δq₁₁ = 0.076
Δρ₁₂, ΔE_{orb} = -2.0, Δq₁₂ = 0.075
Δρ₁₃, ΔE_{orb} = -1.6, Δq₁₃ = 0.066
Δρ₁₄, ΔE_{orb} = -1.5, Δq₁₄ = 0.064
Δρ₁₅, ΔE_{orb} = -1.4, Δq₁₅ = 0.063

Figure S5 Contours of deformation densities, Δρᵢ(𝑟), describing the interaction between Sn²⁺ and the [2.2.2]Paracyclophane, 1, and the corresponding energy, ΔE_{orb}ᵢ (kcal.mol⁻¹), and charge estimation, Δqᵢ = 𝜈ᵢ(a.u.). Red and blue surfaces indicate density outflow and density inflow, respectively (contour value 0.0003).
Δρ₁, ΔE_{orb₁} = -27.1, Δq₁ = 0.528

Δρ₂, ΔE_{orb₂} = -8.9, Δq₂ = 0.270

Figure S6 Contours of deformation densities, Δρ₁(τ), and the main SFOs contributions of the interacting fragments in Ag⁺-1.
Δρ₁, ΔE_{orb₁} = -38.9, Δq₁ = 0.588

Δρ₄, ΔE_{orb₄} = -8.3, Δq₄ = 0.157

Figure S7 Contours of deformation densities, Δρ₁(r), and the main SFOs contributions of the interacting fragments in Sn^{2+}-1.
Table S1. EDA analysis for Ag\(^{+}\)-1, in its \(\eta^6,\eta^6,\eta^6\) coordination mode.

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<td>Ag-1</td>
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<tr>
<td>(\Delta E^{\text{elstat}})</td>
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<td>(42.4%)</td>
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<td>(\Delta E^{\text{orb}})</td>
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<td>(\Delta E^{\text{Disp}})</td>
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