Electronic Supplementary Information: Chiral effects on the final step of an octahedron-shaped coordination capsule self-assembly

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This document provides additional information on the computational methods.

1 Model electronic Hamiltonian

The full account of the model electronic Hamiltonian for the octahedron-shaped coordination capsule self-assembly is available elsewhere, and only brief summary is presented here. The total energy composed of multi metals and ligands is given by

\[ E_{\text{total}} = \sum_{M} E_{\text{M}}^M + \sum_{M \neq M'} V_{MM'} + V_{\text{ligands}} \]  \hspace{1cm} (S1)

where \( E_{\text{M}}^M \) represents the effective energy of Pd atoms (M) in the field of ligands, which was modeled including the quantum effects. The second term is classical coulomb repulsions between Pd\(^{2+}\) ions and the third term is the intra-molecular and inter-molecular interactions of ligands, modeled by the general Amber force field (GAFF).3

The energy, \( E_{\text{M}}^M \), is obtained as a lowest energy, \( E_{\text{M}}(n_M=1,M) \), by diagonalizing the effective Hamiltonian,

\[ H_{\text{eff}}(R)|\psi(n_M,M)\rangle = E_{\text{M}}(n_M,M)|\psi(n_M,M)\rangle \]  \hspace{1cm} (S2)

where the effective Hamiltonian matrix elements are defined by

\[ H_{IJ}^{\text{eff}} = \langle \Phi_I | H_{\text{eff}}^M | \Phi_J \rangle \]  \hspace{1cm} (S3)

with the total electronic wave function of \( n_M \) th state,

\[ |\psi_{n_M}(r,R)\rangle = \sum_{I}^{45} C_I^{\text{M}}(r,M) |\Phi_I^M(r,R)\rangle. \]  \hspace{1cm} (S4)

Here, \( R \) and \( r \) denote the nuclear and electron coordinates respectively. The total electronic wave function is represented as a linear combination of 45\(^{th}\) configurations of Pd\(^{2+}\), \( \Phi_I \), 45 Slater determinants arising from the 4d\(^{th}\) configurations.

The effective Hamiltonian matrix elements between the \( I \) and \( J \) th configurations are expressed by

\[ H_{IJ}^{\text{eff}} = H_{IJ}^{\text{PLM}} + H_{IJ}^{\text{ES,M}} + H_{IJ}^{\text{EX,M}} + H_{IJ}^{\text{CT,M}}. \]  \hspace{1cm} (S5)

The first term correspond to the isolated Pd\(^{2+}\) term and is determined by the experimental values of the Racah parameters. The remaining terms are electrostatic (ES), exchange (EX), charge transfer (CT) interactions between Pd\(^{2+}\) and ligands. These three terms are formulated and parameterized with the aid of perturbation theory.1 The parameters were determined to reproduce the high level electronic structure theoretical results of the elementary ligand exchange reaction of [PdPy\(_4\)]\(^{2+}\) with free Py and the DFT calculations for the formation energies of the various types of species [Pd\(\text{L}_3\text{Py}\)]\(^{2+}\). The model enables us to evaluate the potential energy of the present self-assembly system with adequate accuracy, which is difficult by the generic force field.

2 OPTIM: A program for optimizing geometries and calculating pathways

The model electronic Hamiltonian was combined with the energy landscape exploration program, OPTIM.4,5 OPTIM includes a wide variety of efficient geometry optimization tools for locating stationary points on potential energy surfaces and calculating reaction pathways, without requiring the time-consuming Hessian evaluation. This combination enables us to detect the transition states and local minima of large molecular systems, which is difficult by the electronic structure calculations. The description of the reactions with local minima and transition states connecting them is a traditionally useful approach even to the long-time phenomena which is beyond the scope of the direct molecular dynamics simulation.

The procedure of investigating reaction paths in the present...
study is summarized as follows. Firstly, two local minima to be connected by the transition state were prepared. The geometry of $[\text{Pd}_6\text{L}_8\text{Py}]^{12+}$ close to the Int II in the main manuscript was obtained by attaching one Py toward the one Pd center in the optimized geometry of the product $[\text{Pd}_6\text{L}_8]^{12+}$ and then re-optimizing the geometry of the total system. The geometry of $[\text{Pd}_6\text{L}_8\text{Py}]^{12+}$ close to the Int I in the main manuscript was obtained by trial and error; breaking one bond between Py group in L and Pd$_2^+$ by changing related several dihedral angles of the L, and inserting one new Py instead to make new bond with Pd$_2^+$. The stabilized geometry was obtained with the aid of geometry relaxation by the molecular dynamics simulation. These two geometries close to the Int I and Int II were used as two initial local minima to be connected by the transition state using the OPTIM as explained below. It should be noted that several new local minima with slight different energies were detected during the OPTIM procedure and only lowest ones were reported in the main manuscript as Int I and Int II, since all the energies of Int I, TS and Int II were shifted uniformly with the same character in chirality.

In the OPTIM procedure, the transition states connecting local minima were detected as follows. The doubly-nudged$^6$ elastic band$^7$ method (DNEB) was used to identify likely candidates for transition states between pairs of minima, and then the candidates were tightly converged to geometries with a single negative Hessian eigenvalue using a hybrid eigenvector-following approach$^8$. Intrinsic reaction coordinate (IRC) paths from the obtained transition state geometry were computed in both forward and backward directions. All energy minimizations employ a modified version of Nocedal's L-BFGS algorithm$^9$. All minima and transition states were converged to a tolerance of $10^{-5}$ a.u. for the root mean square gradient. Finally, the keywords and parameters used in the present OPTIM calculation are listed.

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## KEYWORDS & PARAMETERS ##
NEWCONNECT 100 1 20.0 20.0 30 0.0 0.025
NEWNEB 50 500 0.025
NEBK 10.0
DLKSTRA 1
BFGSTS 50 3 25 0.0001
EDIFFTOL 1.0D-6
GEOMDIFFTOL 0.2
BFGSMIN 1.0D-5
UPDATES 10 10
PUSHOFF 0.02
MAXBFGS 0.2 0.2
STEPS 200
MAXSTEP 0.1
MAXMAX 0.2
TRAD 0.2
PATH 1000 0.0
BFGSTEPS 99999
RADIUS 999.0
NOHESS
DUMPALLPATHS
REOPTIMIZEENDPOINTS
## KEYWORDS & PARAMETERS ##
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References