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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.

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1 Model electronic Hamiltonian

The full account of the model electronic Hamiltonian¹ for the octahedron-shaped coordination capsule self-assembly is available elsewhere², and only brief summary is presented here. The total energy composed of multi metals and ligands is given by

$$E_{\text{total}} = \sum_{M} E_{\text{eff}}^{M} + \sum_{M < M'} V_{MM'} + V_{\text{ligands}}$$
(S1)

where $E_{\rm eff}^M$ 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 Pd²⁺ ions and the third term is the intra-molecular and intermolecular interactions of ligands, modeled by the general Amber force field (GAFF)³.

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

$$\boldsymbol{H}_{\text{eff}}^{M}(\boldsymbol{R})\boldsymbol{C}^{(n_{M},M)}(\boldsymbol{R}) = E_{(n_{M},M)}(\boldsymbol{R})\boldsymbol{C}^{(n_{M},M)}(\boldsymbol{R})$$
(S2)

where the effective Hamiltonian matrix elements are defined by

$$H_{IJ}^{\text{eff},M} = \langle \Phi_I^M | \hat{H}_{\text{eff}}^M | \Phi_J^M \rangle \tag{S3}$$

with the total electronic wave function of n_M th state,

$$|\Psi_{n_M}^M(\boldsymbol{r};\boldsymbol{R})\rangle = \sum_{I=1}^{45} C_I^{(n_M,M)}(\boldsymbol{R}) |\Phi_I^M(\boldsymbol{r};\boldsymbol{R})\rangle.$$
(S4)

Here, R and r denote the nuclear and electron coordinates re-

spectively. The total electronic wave function is represented as a linear combination of $4d^8$ configurations of Pd^{2+} , Φ_I , 45 Slater determinants arising from the 4d⁸ configurations.

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

$$H_{IJ}^{\text{eff},M} = H_{IJ}^{\text{Pd},M} + H_{IJ}^{\text{ES},M} + H_{IJ}^{\text{EX},M} + H_{IJ}^{\text{CT},M}.$$
 (S5)

The first term correspond to the isolated Pd²⁺ 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 theory¹. 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 $[Pd_aL_bPy_c]^{2a+}$. 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





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study is summarized as follows. Firstly, two local minima to be connected by the transition state were prepared. The geometry of $[Pd_6L_8Py]^{12+}$ 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 $[Pd_6L_8]^{12+}$ and then re-optimizing the geometry of the total system. The geometry of $[Pd_6L_8Py]^{12+}$ 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 Pd²⁺. 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-nudged⁶ elastic band⁷ 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 approach⁸. 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 algorithm⁹. 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.

KEYWORDS & PARAMETERS ## NEWCONNECT 100 1 20.0 20.0 30 0.0 0.025 NEWNEB 50 500 0.025 **NEBK 10.0** DIJKSTRA 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 **BFGSSTEPS 99999 RADIUS 999.0** NOHESS DUMPALLPATHS REOPTIMISEENDPOINTS ## KEYWORDS & PARAMETERS

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