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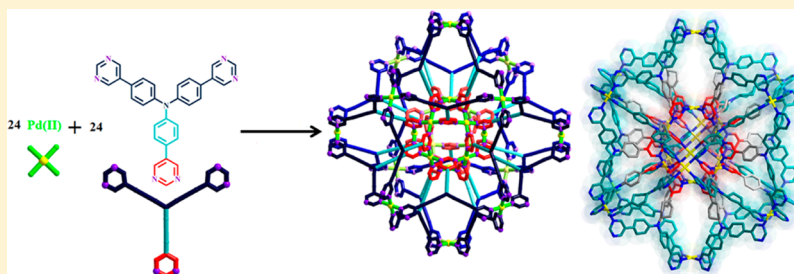
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A Pd₂₄ Pregnant Molecular Nanoball: Self-Templated Stellation by Precise Mapping of Coordination Sites

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S Supporting Information



ABSTRACT: We found that Pd(II) ion (M) and the smallest 120° bidentate donor pyrimidine (L_a) self-assemble into a mononuclear $M(L_a)_4$ complex (**1a**) instead of the expected smallest $M_{12}(L_a)_{24}$ molecular ball (**1**), presumably due to the weak coordination nature of the pyrimidine. To construct such a pyrimidine bridged nanoball, we employed a new donor tris(4-(pyrimidin-5-yl)phenyl)amine (L); which upon selective complexation with Pd(II) ions resulted in the formation of a pregnant $M_{24}L_{24}$ molecular nanoball (**2**) consisting of a pyrimidine-bridged Pd_{12} baby-ball supported by a Pd_{12} larger mother-ball. The formation of the baby-ball was not successful without the support of the mother-ball. Thus, we created an example of a self-assembly where the inner baby-ball resembling to the predicted $M_{12}(L_a)_{24}$ ball (**1**) was incarcerated by the giant outer mother-ball by means of geometrical constraints. Facile conversion of the pregnant ball **2** to a smaller $M_{12}(L_b)_{24}$ ball **3** with dipyridyl donor was achieved in a single step.

INTRODUCTION

Inspired by the incredible emergence of precise assembly in well-defined large structures of multiple proteins subunits,¹ chemists have explored various creative approaches to prepare polyhedral molecular architectures with specific Platonic and Archimedean geometries having desired functions.² Careful control over coordination interaction of exomultidentate ligands with transition metal ions has been pursued with special attention to fabricate several topologically similar derivatives such as “cubes”,³ “balls”,⁴ and “spheres”⁵ with structural resemblance to spherical virus capsids. Since the vertices and edges of these architectures are occupied by metal ions and organic ligands respectively, understanding the underlying principles is crucial to effectively map a particular structure by designing appropriate donor and acceptor units.⁶ However, due to relatively flexible and weak nature of the coordination bond, sometimes other factors (e.g., template,⁷ solvents,⁸ bent angle,⁹ etc.) may influence the self-assembly leading to unprecedented architectures. For example, Fujita and co-workers have shown that slight change in ligand bent angle can result into incommensurable difference in the final structures; from cuboctahedron to rhombicuboctahedron.⁹ Therefore, a more precise understanding of the interplay of these several effects is necessary for the preparation of desired architectures by control self-assembly.

On the other hand, supramolecular self-selection depends on specific instructions like coordination environment of metal ions,¹⁰ steric constraints,¹¹ and geometrical complementarity¹² which are encoded in building components. This represents a novel approach to build-up functionally integrated and structurally organized supramolecular architectures from multiple subunits. Moreover, lability of coordination interactions allows reversible associations of the building units by continuous exchange which is associated with error-checking and thus often leads to the formation of predominant thermodynamic product(s).¹³ Several external stimuli, like solvent,¹⁴ pH¹⁵ and temperature,¹⁶ can sometimes also decide the fate of certain recognition process. However, influence of electronic properties of the subunits and entropic factor to guide such self-selection process in complex mixture of competing species has been investigated in limited number of systems.^{17,18}

Based on the previous results,^{19a} the outcome of the self-assembly of a square planar Pd(II) ion with any 120° bidentate rigid donor (X) should be a $Pd_{12}X_{24}$ cuboctahedral cage. Pyrimidine (L_a) is considered to be the shortest 120° bidentate donor with two donor nitrogens separated by a single carbon atom. Hence, self-assembly of pyrimidine (L_a) with square

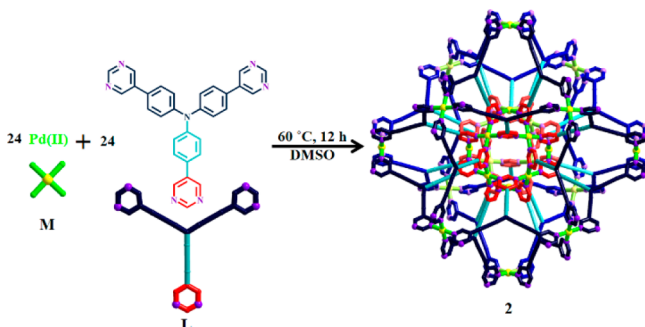
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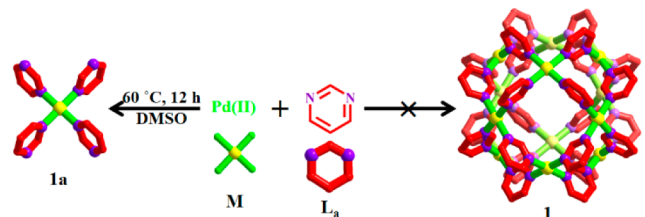


planar naked Pd(II) should lead to the formation of smallest $M_{12}(L_a)_{24}$ cuboctahedron (1) (Scheme 2). Herein, we report the formation of a simple mononuclear $M(L_a)_4$ complex (1a) by two-component self-assembly of Pd(II) ion (M) and pyrimidine (L_a) instead of anticipated $M_{12}(L_a)_{24}$ molecular sphere (Scheme 2). Interestingly, an analogous spherical pyrimidine bridged smallest cuboctahedron was possible to form with the support of a larger cage employing a new donor L (L = tris(4-(pyrimidin-5-yl)phenyl)amine) (Scheme 1). This

Scheme 1. Synthesis of Stellated $M_{24}L_{24}$ Pregnant Coordination Cage (2) by Two-Component Self-Assembly



Scheme 2. Schematic Representation of the Formation of $M(L_a)_4$ Mononuclear Complex (1a) Instead of Expected $M_{12}(L_a)_{24}$ Molecular Sphere (1) by Two-Component Self-Assembly



expanded tripyrimidine donor led to the formation of a pregnant $M_{24}L_{24}$ molecular nanoball (2) upon simple treatment with naked Pd(II) ions. To the best of our knowledge, this is the first example where we show that formation of a baby-cage $M_{12}(L_a)_{24}$ is possible only in the womb of an analogous larger outer cage (mother-cage) which induces stability through templation.

RESULTS AND DISCUSSION

Synthesis and Characterization of 1a. Previously, Fujita and colleagues pioneered the use of coordination interactions to preorganize 24 bidentate bent pyridyl ligands (X) around 12 Pd(II) ions to prepare $M_{12}X_{24}$ spherical discrete architectures.¹⁹ Such type of coordination in structurally related simple 120° donor, pyrimidine (L_a) with Pd(II) ion should, in principle, result in the formation of a small molecular ball $M_{12}(L_a)_{24}$ (Scheme 1). With this notion, we performed self-assembly of Pd(II) ion with pyrimidine in 1:2 ratio in DMSO. Substantial downfield shift was observed in the 1H NMR of the isolated product which is characteristic of coordination to metal. In addition, four aromatic peaks in the proton NMR were inconsistent with the symmetric ball formation (Figure S4). Notably, diffusion-ordered NMR spectroscopy (DOSY) showed a clear single band at $D = 1.3 \times 10^{-10} \text{ m}^2/\text{s}$ ($\log D = -9.89$), which is higher as compared to that previously reported

for $M_{12}X_{24}$ type cuboctahedron (Figure S4). Finally, appearance of prominent peaks at $m/z = 488.2 [1a - NO_3^-]^{1+}$ and 213.5 $[1a - 2NO_3^-]^{2+}$ in ESI-MS analysis apparently indicated the formation of [1 + 4] self-assembled product. Finally, the single-crystal X-ray study affirmed that the solid-state structure of 1a to be consistent with the structure proposed based on solution phase NMR and ESI-MS analyses (Figure 3). Diffraction quality block-shaped yellow single-crystals were obtained by slow vapor diffusion of acetone into the concentrated DMSO solution of the assembly.

Structural refinements revealed that complex 1a crystallized in triclinic system with $P\bar{1}$ space group. It has C_{2h} point group symmetry. The asymmetric unit consists of one palladium and four pyrimidine units, and the average Pd–N bond length is in the range of 2.02–2.03 Å. One of the coordination sites of pyrimidine participates in complexation to form $M(L_a)_4$ complex leaving other site uncoordinated.

To obtain quantitative insight into the energetics of the reactions, we performed theoretical calculations. Although, solvent effects and electrostatic interactions play essential roles in the stability of the self-assembled products, it is very difficult to estimate the energetics of the reaction process by taking account these factors. Therefore, to compare the heat of reactions, a compromise was made by estimating the energy differences between the products and reactants. The energy of the involved components were optimized through DFT (B3LYP) calculations (Figure S7). In both cases, the calculated heat of reactions were found to be positive, indicating significant contribution from solvent effects and electrostatic interactions in the product formations. The calculation predicts that the formation cuboctahedron (1) is more energy demanding (11 923.4 kcal/mol) as compared to the mononuclear complex (1a) (232.7 kcal/mol). In other words, each Pd center in complex 1a gains an extra -760.9 kcal/mol stability (Scheme S2). So, the formation of the $M_{12}(L_a)_{24}$ ball was energetically unfavored.

Self-Templation. The ability of a template to induce stability in an otherwise unstable molecule has many interesting consequences. For instance, the formation of dynamic library of coordination complexes in the presence of appropriate anionic template has been reported earlier.⁷ We, therefore, speculated that the synthesis of such pyrimidine bridged small nanoball might be possible by stabilizing it through templation effects. To verify the feasibility of our approach, we first designed and synthesized a new exohexadentate ligand L comprising triphenylamine core in 87% yield by Suzuki coupling of tris(4-bromophenyl)amine and pyrimidine-5-boronic acid at 85 °C (Scheme S1). The hexadentate ligand was characterized by various spectroscopic techniques (Figures 2 and S1–S3). The ligand is almost coplanar and both the ligand and metal ions have divergent coordination modes. It is therefore expected to generate polymeric product if all aromatic nitrogen ligate to naked Pd(II) ion. However, complexation of L with $Pd(NO_3)_2$ in 1:1 molar ratio in DMSO resulted a clear yellow solution. Our first impression was that the reaction led to the formation of a discrete complex instead of polymeric product. Since, $Pd(NO_3)_2$ has divergent coordination sites, the structural convergence is only possible if the ligand uses A and B sites for coordination leaving C site uncomplexed (Figure 1) to result in a complex structure. On the other hand, coordination interaction of C site with $Pd(NO_3)_2$ can lead to the formation of “paddle wheel”²⁰ structure (Pd_2L_4) where A and B sites (Figure 1) remain uncoordinated. The product was isolated as

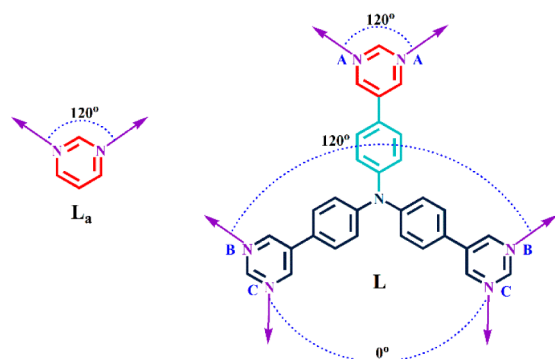


Figure 1. Different coordination sites of the donors.

yellow precipitate by triturating the reaction mixture with excess amount of cold acetone. Noticeable downfield shifts particularly for pyrimidine rings were observed in the proton NMR signals which were quite broad at room temperature. This was ascribed to the slower tumbling motion of very large assembly as compared to NMR time scale (Figure 2). The

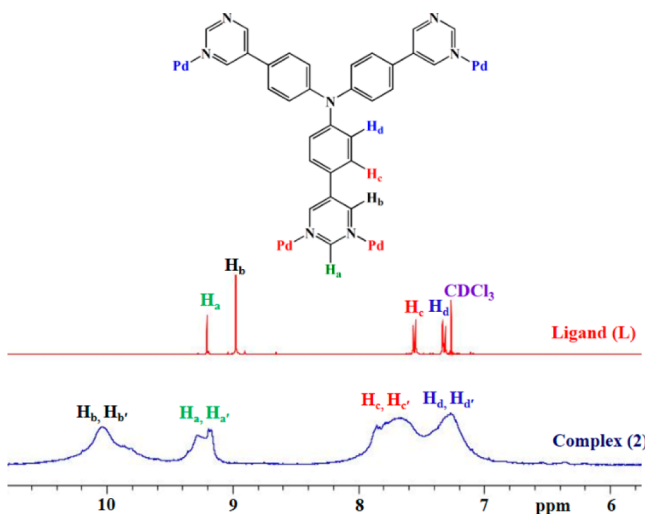


Figure 2. Partial ^1H NMR spectra of the ligand **L** (top) recorded in CDCl_3 and $\text{M}_{24}\text{L}_{24}$ pregnant molecular nanoball (**2**) (bottom) recorded in $\text{DMSO}-d_6$.

magnetically nonequivalent pyrimidine rings in each ligand (**L**) displayed two sets of peaks, as observed in ^1H NMR spectra. Furthermore, a clear single band was encountered in DOSY NMR spectra at $D = 7.8 \times 10^{-11} \text{ m}^2/\text{s}$ ($\log D = -10.11$) which is much smaller than that of free ligand $D = 1.1 \times 10^{-9} \text{ m}^2/\text{s}$ ($\log D = -8.96$) (Figure S5), apparently indicating the formation of much larger structure. Due to the high molecular weight and relatively weak Pd–N bonds, mass analysis of the complex was extremely difficult. Nevertheless, after optimizing the condition, ESI-MS analysis showed a prominent peak at $m/z = 1357.1$ presumably due to the $[\text{2} - 12\text{NO}_3]^{12+}$ fragment (Figure S6).

Structural conformation of the double layered $\text{M}_{24}\text{L}_{24}$ stellated assembly (**2**) was subsequently obtained by X-ray crystallographic analysis where selective coordination was observed at sites A and B, while sites C remained uncoordinated (Figure 3). Complex **2** crystallized in tetragonal system with space group $I4/m$. It possesses approximate T_h point symmetry. Three Pd(II) ions and four ligands are present

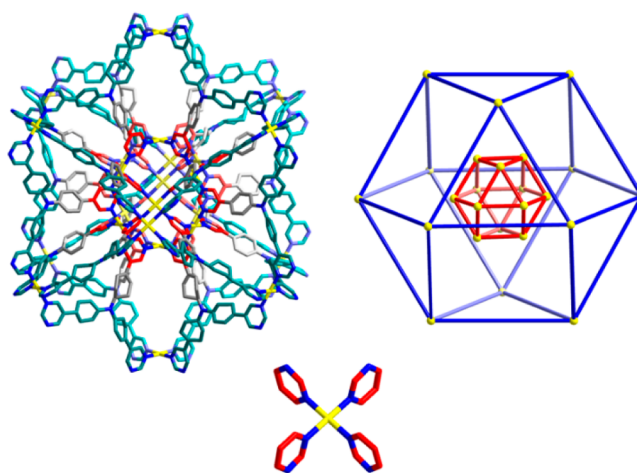
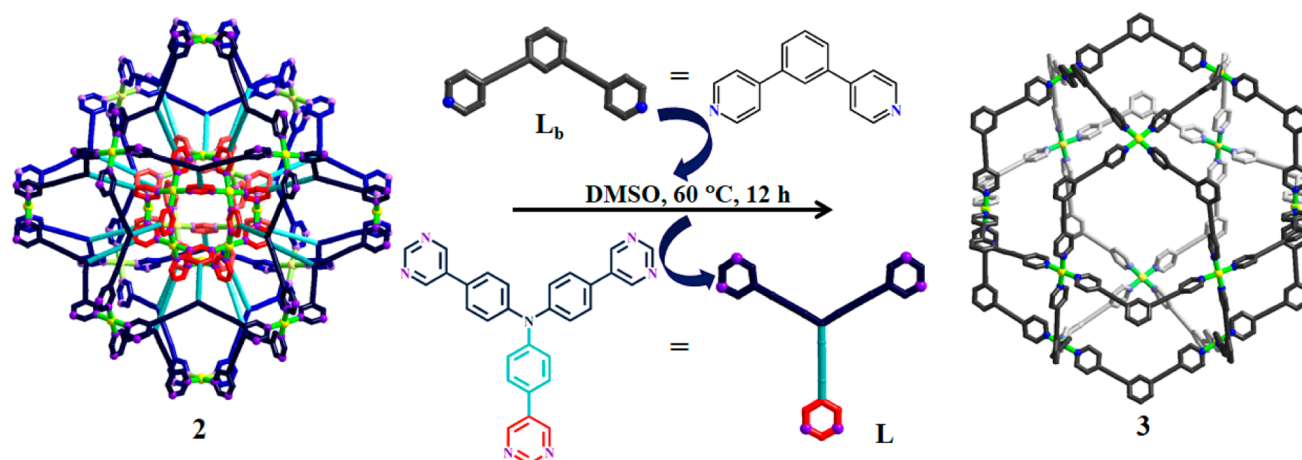


Figure 3. X-ray structure of the complexes **2** (left) and **1a** (bottom) and stripped down version of the structure **2** defining cuboctahedral framework (right). (Color codes: Pd = yellow, N = blue, C = red, gray, and sky blue.) Hydrogen atoms and counteranions are omitted for clarity.

in the asymmetric unit. Both cuboctahedral frameworks (inner and outer) consist of six square and eight triangular windows. Twelve clipping Pd(II) ions are, in fact, connected by one of the coordination sites of the extended arms of pyrimidine to form stellated complex **2**. The framework contains void space with the separation between most distant Pd(II) ions is about 36.10 Å. It also has six square and eight triangular concave surfaces with the diameter of the inscribed circles being about 18.01 and 5.61 Å, respectively, which suggested that the architecture could potentially act as different functional domains. More importantly, the outer ball acts as a template and induces stability to the inner ball, which is an analogue of **1**. The pyrimidine bridged inner baby-ball was not formed at all when Pd(II) was separately treated with free pyrimidine. Formation of this baby-ball was only possible in the presence of the support of the larger mother ball formed by the coordination sites B of **L** (Figure 1). Thus, the overall structure of the final architecture can be considered as “pregnant molecular nanoball” with a Pd₁₂ baby-ball in the womb of a Pd₁₂ mother-ball.

Self-Selection. Although pyridyl donors are widely employed to build coordination cages, pyrimidine-based donors are important owing to their versatile coordination behavior despite their weaker donating ability. We envisaged that this kind of electronic information can determine the outcome of selection process involving mixture of pyrimidine- and pyridine-based competing components. To investigate this, we performed a competitive experiment by subjecting a mixture of 1,3-dipyridylbenzene (**L_b**) and pyrimidine-based donors (**L**) to interact with acceptor Pd(II) ions (**M**) in 2:1:1 ratio in DMSO at 60 °C (Scheme S4). The low ligand strength of pyrimidine allows the acceptor **M** to selectively bind with **L_b** to form molecular $\text{M}_{12}(\text{L}_b)_{24}$ ball (**3**),^{19a} leaving **L** unreacted, as evidenced by the ^1H NMR spectra of the isolated product (Figure S8). To further establish the self-recognition process, we performed cage-to-cage conversion experiment by adding **L_b** in an incremental fashion into the solution of **2** at 60 °C (Scheme 3). Accordingly, the product was precipitated out and the progress of the reaction was monitored by ^1H NMR spectroscopy. Analysis of proton signals depicted that gradual addition of **L_b** led to the depletion of broad peaks

Scheme 3. Conversion of Pregnant Molecular Nanoball (2) to Preferred Nanoball (3) Containing Pyridyl Donor with the Addition of Appropriate Ligand (L_b)



corresponding to 2, followed by the simultaneous appearance of a band of peaks ascribed to the mixture of 3 and L. A complete disappearance of broad proton signal at 10.01 ppm upon 100% addition of L_b confirmed that the pregnant nanoball 2 fully transformed into spherical complex 3 as a preferred product and L remained uncoordinated in solution (Figure S9). Thus, the preferred constituents self-organized to form the thermodynamically most stable product even though both pyrimidine and pyridine donors were present in the reaction mixture. Such self-selection and cage-to-cage transformation are presumably governed by higher donating ability of pyridine as well as entropic factor of the assembly process.

CONCLUSIONS

In summary, to investigate the versatility of 120° ditopic donors on square planar Pd(II), we employed simple pyrimidine (L_a) as smallest 120° donor with Pd(II). Surprisingly, such self-assembly of $Pd(NO_3)_2$ and pyrimidine (L_a) led to the formation of a mononuclear $Pd(L_a)_4$ complex instead of expected $Pd_{12}(L_a)_{24}$ molecular ball, presumably due to weak coordination ability of free pyrimidine. To circumvent this problem, we have converted pyrimidine to an expanded new tripyrimidine donor L. Self-assembly of L with square planar Pd(II) yielded a very large pregnant molecular nanoball $Pd_{24}L_{24}$ consisting of pyrimidine-bridged Pd_{12} baby-ball supported by an outer Pd_{12} larger mother-ball. The smaller Pd_{12} nanoball bridged by pyrimidine was not formed when Pd(II) was treated with pyrimidine alone. The existence of such Pd_{12} baby-nanoball was realized only inside an analogous larger Pd_{12} ball. The present results establish the role of supporting large structure in stabilizing analogous smaller structure by self-templation. Finally, the weak coordination ability of the pyrimidine moiety was utilized for self-selection and cage-to-cage transformation by converting the pregnant Pd_{24} nanoball (2) to a relatively smaller Pd_{12} nanoball (3) in a facile manner. The strategy used here for the synthesis of double-shell superstructure establishes new guidelines for the creation of novel complex architectures.

EXPERIMENTAL SECTION

General Procedures. All the chemicals were purchased from commercial sources and used without further purification. Tris(4-bromophenyl)amine and cage 3 were synthesized following the reported procedure.²¹ The NMR spectra were recorded on Bruker 400

MHz instrument. The chemical shifts (δ) in the 1H NMR spectra are accounted in ppm relative to tetramethylsilane (Me_4Si) as internal standard (0.0 ppm) or proton resonance resulting from incomplete deuteration of the solvent $(CD_3)_2SO$ at (2.51 ppm) and $CDCl_3$ (7.26 ppm). Electrospray ionization mass spectrometry (ESI-MS) experiments were carried out in Bruker Daltonics (Esquire 300 Plus ESI model) using standard spectroscopic grade solvents acetonitrile and methanol. Elemental analyses (C, H, N) were performed using a PerkinElmer 240C elemental analyzer. IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer.

Synthesis of Tris(4-(pyrimidin-5-yl)phenyl)amine (L). A mixture of tris(4-bromophenyl)amine (500.0 mg, 1.04 mmol), pyrimidine-5-boronic acid (578.0 mg, 4.66 mmol), $Pd(PPh_3)_4$ (59.5 mg, 5.0 mol %), and K_2CO_3 (1.38 g, 10.0 mmol) was taken in 50 mL of THF and water (5:1) mixture and refluxed under the nitrogen atmosphere. After 48 h, the reaction mixture was extracted with chloroform and the product was purified by column chromatography. Isolated yield: 60%. Anal. calcd for (activated sample) $C_{30}H_{21}N_7$: C, 75.14; H, 4.41; N, 20.45. Found: C, 74.78; H, 4.79; N, 20.42. IR: ν (cm^{-1}) = 3028, 1596, 1547, 1270, 830, 723, 556. 1H NMR (400 MHz, $CDCl_3$): δ = 9.20 (s, 3H), 8.96 (s, 6H), 7.55 (d, 6H), 7.31 (d, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.38, 154.64, 147.82, 133.71, 129.39, 128.25, 125.17. HRMS calcd for $C_{30}H_{21}N_7H$ [$M + H$]⁺ m/z = 480.1937, found 480.1911.

General Procedure for the Synthesis of Complexes 1a and 2. A DMSO solution (2 mL) of $Pd(NO_3)_2$ was added to the individual solid ligand (L_a/L), and the reaction mixture was stirred at 60 °C. After 12 h, product (1a/2) was obtained with the addition of excess amount of ethyl acetate.

Synthesis of Complex 1a. DMSO solution of $Pd(NO_3)_2$ (10.0 mg, 0.043 mmol) was added into pyrimidine (L_a) (6.9 mg, 0.086 mmol). Isolated yield: 45%. Anal. calcd for (activated sample) $C_{16}H_{16}N_{10}O_6Pd$: C, 34.89; H, 2.93; N, 25.43. Found: C, 35.31; H, 3.02; N, 26.24. IR: ν (cm^{-1}) = 3065, 1595, 1311, 926, 697, 640. 1H NMR (400 MHz, $(CD_3)_2SO$): δ = 9.77 (s, 1H), 9.34 (d, 1H), 8.96 (d, 1H), 7.81 (t, 1H). ESI-MS (m/z) = 488.2 [$1a - NO_3^-$]⁺ and 213.5 [$1a - 2NO_3^-$]²⁺.

Synthesis of Complex 2. Ligand L (20.8 mg, 0.043 mmol) was added to the DMSO solution of $Pd(NO_3)_2$ (10.0 mg, 0.043 mmol). Yield: 90%. Anal. calcd for (activated sample) $C_{720}H_{504}N_{216}O_{144}Pd_{24}$: C, 50.75; H, 2.98; N, 17.76. Found: C, 51.17; H, 3.31; N, 18.43. IR: ν (cm^{-1}) = 3074, 2159, 1594, 1506, 1266, 827, 702, 560. 1H NMR (400 MHz, $(CD_3)_2SO$): δ = 10.01 (bs, 144H), 9.19 (bs, 72H), 7.81 (bd, 144H), 7.27 (bd, 144H). ESI-MS (m/z) = 1357.1 [$2 - 12NO_3^-$]¹².

Self-Recognition Experiment ($M + L_b + L$). A DMSO solution (1 mL) of $Pd(NO_3)_2$ (5.0 mg, 0.022 mmol) was added to the solid mixture of L_b (10.1 mg, 0.043 mmol) and L (10.4 mg, 0.022 mmol). The resulting mixture was stirred at 60 °C for 12 h, and the product

was obtained by the addition of ethyl acetate to the reaction mixture. Preferential binding with appropriate ligand was investigated by ^1H NMR spectroscopy.

Cage-to-Cage Transformation. Ligand **L_b** (9.8 mg, 0.042 mmol) was added gradually to the DMSO solution (1 mL) of cage **2** (15.0 mg, 0.0009 mmol) with subsequent stirring at room temperature for 20 min, and the reaction was monitored by ^1H NMR spectroscopy. After 100% addition, the reaction mixture was kept for stirring at 60 °C for 6 h. Finally, the product was purified by triturating with excess amount of ethyl acetate.

X-ray Data Collection and Structure Refinements. The diffraction data of **1a** was accumulated on a Bruker SMART APEX CCD diffractometer and complex **2** with synchrotron radiation. Data reduction was performed by using the SMART/SAINT software.²² Intensity data were collected using graphite-monochromatic Mo $K\alpha$ radiation (0.7107 Å) at 100 K on a crystal as obtained after several attempts. The structures were solved by direct methods using SHELX-2013²³ incorporated in WinGX.^{24–26} Empirical absorption corrections were applied with SADABS.²⁷ All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were assigned isotropic displacement coefficients, $U(\text{H}) = 1.2U(\text{C})$ or $1.5U(\text{C-methyl})$, and their coordinates were allowed to ride on their respective carbons. The quality of the obtained X-ray data was poor due to the presence of severely disordered solvent molecules and counteranions. Therefore, for complexes **2**, refinement was carried out constraining a few bond distances fixed using DFIX command and final refinement was performed with the modification of the structure factors for the electron densities of the solvent molecules and counteranions using SQUEEZE option of PLATON.²⁷

Crystal Data for 1a. $\text{C}_{16}\text{H}_{16}\text{N}_{10}\text{O}_6\text{Pd}$; $M_r = 550.79$, triclinic $P\bar{1}$, $a = 7.9119(7)$ Å, $b = 10.6627(9)$ Å, $c = 12.1631(10)$ Å, $\alpha = 84.422(2)^\circ$, $\beta = 85.326(2)^\circ$, $\gamma = 88.627(2)^\circ$, $V = 1017.72(15)$ Å³, $Z = 2$, Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å), $T = 100(2)$ K, $R1 = 0.0384$, $wR2 = 0.1136$ ($I > 2\sigma(I)$).

Crystal Data for 2. $\text{C}_{720}\text{H}_{1306}\text{N}_{216}\text{O}_{577}\text{Pd}_{24}$; $M_r = 24774.94$, tetragonal $I4/m$, $a = 36.935(5)$ Å, $b = 36.935(5)$ Å, $c = 53.156(11)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 72515(25)$ Å³, $Z = 2$, Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å), $T = 100(2)$ K, $R1 = 0.0869$, $wR2 = 0.2698$ ($I > 2\sigma(I)$).

Computational Methods. Full geometry optimizations were performed employing the Gaussian 09 package.²⁸ The hybrid B3LYP functional has been utilized in all calculations as implemented in the Gaussian 09 package, mixing the exact Hartree–Fock-type exchange with Becke's expression for the exchange functional²⁹ and that proposed by Lee–Yang–Parr for the correlation contribution.³⁰ The LANL2DZ basis set was utilized for all of the calculations.

■ ASSOCIATED CONTENT

● Supporting Information

Characterization data (NMR, FTIR, ESI-MS) of the complexes. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06628.

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Notes

The authors declare no competing financial interest.

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