

Geometric Complementarity in Assembly and Guest Recognition of a Bent Heteroleptic cis - $[Pd_2L^A_2L^B_2]$ Coordination Cage

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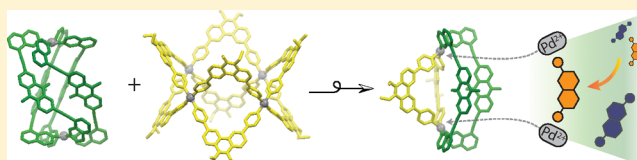
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S Supporting Information

ABSTRACT: Due to the inherent difficulties in achieving a defined and exclusive formation of multicomponent assemblies against entropic predisposition, we present the rational assembly of a heteroleptic $[Pd_2L^A_2L^B_2]^{4+}$ coordination cage achieved through the geometric complementarity of two carefully designed ligands, L^A and L^B . With Pd(II) cations as rigid nodes, the pure distinctly angular components readily form homoleptic cages, a $[Pd_2L^A_4]^{4+}$ strained helical assembly and a $[Pd_4L^B_8]^{8+}$ box-like structure, both of which were characterized by X-ray analysis. Combined, however, the two ligands could be used to cleanly assemble a cis - $[Pd_2L^A_2L^B_2]^{4+}$ cage with a bent architecture. The same self-sorted product was also obtained by a quantitative cage-to-cage transformation upon mixing of the two homoleptic cages revealing the $[Pd_2L^A_2L^B_2]^{4+}$ assembly as the thermodynamic minimum. The structure of the heteroleptic cage was examined by ESI-MS, COSY, DOSY, and NOESY methods, the latter of which pointed toward a cis -conformation of ligands in the assembly. Indeed, DFT calculations revealed that the angular ligands and strict Pd(II) geometry strongly favor the cis - $[Pd_2L^A_2L^B_2]^{4+}$ species. The robust nature of the cis - $[Pd_2L^A_2L^B_2]^{4+}$ cage allowed us to probe the accessibility of its cavity, which could be utilized for shape recognition toward stereoisomeric guests. The ability to directly combine two different backbones in a controlled manner provides a powerful strategy for increasing complexity in the family of $[Pd_2L_4]$ cages and opens up possibilities of introducing multiple functionalities into a single self-assembled architecture.



INTRODUCTION

Inspired by the function and complexity of biological systems, the design of artificial supramolecular host assemblies has become a burgeoning area of study, particularly utilizing the powerful tool of coordination-driven self-assembly from ligand and metal building blocks.¹ The adjustable cavity of resulting assemblies has produced host systems capable of acting as chemical sensors,² drug transporters,³ components of complex systems,⁴ stabilization media,⁵ and more.^{1c,6} Much of this, however, has been achieved by relatively simple homoleptic assemblies consisting of one type of ligand. For the purpose of approaching greater complexity and functionality, the derivation of strategies to control the arrangement of different ligand entities in a single assembly is an area that has recently received much attention.⁷ For example, Zheng and Stang's charge separation,⁷ⁿ Schmittl's steric constraints^{7s} and Fujita's side chain-directed approach^{7r} are among some of the proven methods to access both complex and functional heteroleptic metallosupramolecular architectures.⁸

$[M_2L_4]$ coordination cages assembled from square-planar metal cations such as Pd(II), Pt(II), Cu(II), and Ni(II) and banana-shaped bis-monodentate ligands are a family of robust and diverse molecular hosts with the ability to provide

accessible cavities due to their symmetric and spatial arrangement of ligands.⁹ The properties of the most intensively studied $[Pd_2L_4]$ cages are often imparted through functionalization of the ligand components, a strategy that has yielded assemblies with attractive properties such as selective guest binding,^{3b,10} stimuli responsive structural transitions¹¹ or rearrangements,¹² redox properties,¹³ and biological activity.¹⁴ However, there still remains great scope to extend the complexity and functionality of these architecturally simple assemblies by incorporating more than one type of ligand entity into the structure. Controlled formation of heteroleptic $[Pd_2L_2L'_2]^{4+}$ assemblies from unprotected Pd(II) cations however has seldom been reported; often the combination of a metal ion with two or more distinct ligands leads to uncontrolled statistical mixtures or narcissistic self-sorting,¹⁵ especially in the case of N-donor coordinated Pd(II).¹⁶ Nevertheless, some examples exist: Johnson and Hooley reported a degree of control over the formation of heteroleptic cages by endohedral functionalization of banana-shaped ligands with differing degrees of steric bulk. A 1:1 mixture of a $[Pd_2L_4]^{4+}$ and $[Pd_2L_3L'_1]^{4+}$ species could be

Received: August 22, 2016

Published: September 22, 2016

observed with a combination of bulky and nonbulky ligands.¹⁷ On the other hand, Yoshizawa and co-workers recently reported a $[\text{Pd}_2\text{L}_2\text{L}'_2]^{4+}$ cage achieved through a template effect with a C_{60} guest.¹⁸ While these systems nicely showcase different strategies to achieve heteroleptic assemblies, they suffer from the problem that their formation is inevitably linked to an already occupied cavity.

Most recently, Crowley and co-workers reported a strategy to achieve controlled formation of $[\text{Pd}_2\text{L}_2\text{L}'_2]^{4+}$ coordination cages through exploitation of H-bonding between electron-rich 2-amino substituted pyridyl ligand components.¹⁹ Intriguingly, the kinetically driven heteroleptic assembly could only be accessed through ligand displacement reactions, rather than from direct ligand assembly or cage-to-cage conversion of their homoleptic counterparts. Apart from these examples, strategies to access coordinatively saturated Pd(II) cage assemblies from at least two distinct ligand components remain scarce.

Herein we report the preprogramming of ligand components (L^{A} and L^{B}) with shape complementarity based on a directional bonding approach²⁰ as a robust route to the controlled and template-free formation of a three-component $[\text{Pd}_2\text{L}^{\text{A}}_2\text{L}^{\text{B}}_2]^{4+}$ assembly (C3). In contrast with most previously reported multicomponent assembly strategies,⁷ the formation here does not rely upon the combination of different donor sets or implementation of steric bulk, but rather the energy benefit associated with utilizing ligands of a complementary shape, which results in the heteroleptic assembly as the stable, thermodynamic product.

RESULTS AND DISCUSSION

Synthesis of Ligands L^{A} and L^{B} . Initially, we compared the formation of homo- and heteroleptic self-assemblies based on the two shape complementary ligands L^{A} and L^{B} (Figure 1). Therefore, ligand L^{A} was synthesized by Sonogashira cross-coupling of 2,7-dibromo-10-hexylacridin-9(10*H*)-one with 8-ethynyl-isoquinoline, while ligand L^{B} was prepared by a Suzuki coupling of 3,6-dibromo-9,10-dimethoxyphenanthrene and 4-pyridineboronic acid pinacol ester. The structures of L^{A} and L^{B} were confirmed using NMR spectroscopy, mass spectrometry, and X-ray crystallography (Supporting Information). We then turned our attention to investigating the respective Pd-mediated homoleptic assemblies of L^{A} and L^{B} .

Homoleptic Assembly of Cages C1 and C2 . With regards to L^{A} , we anticipated that the eight inward-pointing isoquinoline donors may have to undergo severe twisting in a $[\text{Pd}_2\text{L}^{\text{A}}_4]^{4+}$ assembly. Heating a 2:1 mixture of L^{A} and $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ in DMSO at 70 °C for 2 h resulted in the quantitative formation of a single product, identified as a $[\text{Pd}_2\text{L}^{\text{A}}_4]^{4+}$ cage (C1) by ^1H NMR spectroscopy (Figure 2b) and mass spectrometry (Figure S27). The ^1H NMR spectrum of C1 revealed a significant upfield shift of several isoquinoline and acridone proton signals of L^{A} (Figure 2a,b), suggesting shielding by a neighboring π -system due to twisting and dense association of the ligand backbones. Indeed the X-ray structure of C1 revealed that the four ligands (two of which are crystallographically unique) are in a highly twisted conformation, participating in either π -stacking or hydrogen bonding with neighboring backbones, resulting in a helical assembly (Figure 5a). Due to packing effects, C1 contains C_2 symmetry in the solid-state; however the number of observed NMR signals indicates that the overall flexibility of the assembly allows for a higher, 4-fold symmetry in solution. Noteworthy is

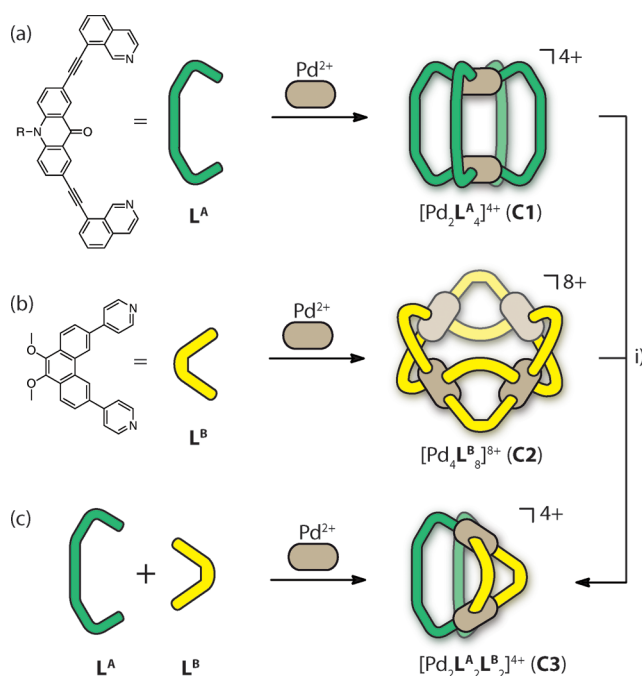


Figure 1. Self-assembly scheme showing the ligands and coordination cages presented in this work: (a) self-assembly of a homoleptic $[\text{Pd}_2\text{L}^{\text{A}}_4]^{4+}$ cage (C1); (b) self-assembly of a homoleptic $[\text{Pd}_4\text{L}^{\text{B}}_8]^{8+}$ box (C2); (c) three-component self-assembly of a heteroleptic $[\text{Pd}_2\text{L}^{\text{A}}_2\text{L}^{\text{B}}_2]^{4+}$ cage (C3), achieved either from the individual ligand components and Pd(II) or by (i) mixing C1 and C2 in a 2:1 ratio.

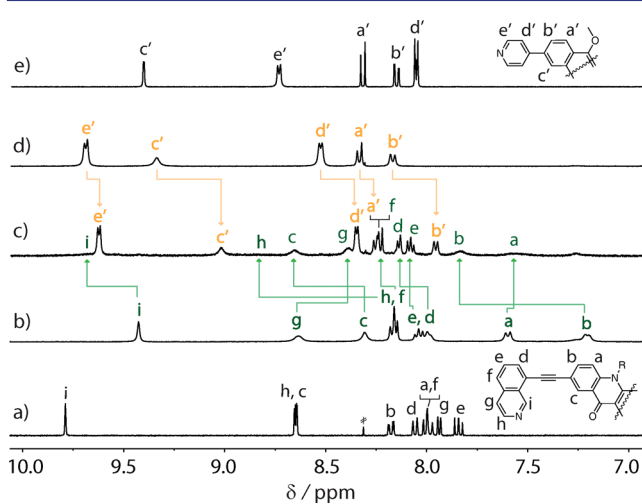


Figure 2. Partial ^1H NMR (400 MHz/DMSO- d_6 , 25 °C) spectra showing the self-assembly of $[\text{Pd}_2\text{L}^{\text{A}}_4]^{4+}$ (C1), $[\text{Pd}_4\text{L}^{\text{B}}_8]^{8+}$ (C2), and $[\text{Pd}_2\text{L}^{\text{A}}_2\text{L}^{\text{B}}_2]^{4+}$ (C3): (a) L^{A} ; (b) $[\text{Pd}_2\text{L}^{\text{A}}_4]^{4+}$ obtained by heating L^{A} with 0.5 equiv of Pd(II); (c) $[\text{Pd}_2\text{L}^{\text{A}}_2\text{L}^{\text{B}}_2]^{4+}$ obtained by heating a 1:1:1 mixture of L^{A} , L^{B} , and Pd(II) or a 2:1 mixture of $[\text{Pd}_2\text{L}^{\text{A}}_4]^{4+}$ and $[\text{Pd}_4\text{L}^{\text{B}}_8]^{8+}$, respectively; (d) $[\text{Pd}_4\text{L}^{\text{B}}_8]^{8+}$ obtained from heating L^{B} and 0.5 equiv of Pd(II); (e) L^{B} .

the compressed nature of the structure, with a Pd...Pd distance of 15.05 Å.

For the Pd-mediated assembly of L^{B} , we expected a different structure due to the para-substituted pyridine donors, which create an approximate 60° vector angle with respect to the phenanthrene backbone. Indeed, heating a 2:1 mixture of L^{B} and $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ in DMSO at 70 °C for 2 h resulted in the quantitative formation of a $[\text{Pd}_4\text{L}^{\text{B}}_8]^{8+}$ (C2) cage species

(Figure 1b). The ESI HR-MS spectrum was consistent with only one major species, yielding signals for ions of $[\text{Pd}_4\text{L}_8 + n\text{BF}_4]^{8-n+}$ ($n = 1-4$) (Figure S28). In the ^1H NMR spectrum, downfield shifts of pyridyl protons H_e and H_d were observed (Figure 2e,d), consistent with Pd(II) complexation. Along with 2D NMR analysis, these observations pointed toward a D_{4h} symmetric M_4L_8 “box” structure for **C2**, a topology that has previously been encountered by Fujita and co-workers using a similar ligand.²¹ The structure of **C2** was confirmed by X-ray crystallography, which revealed the expected connectivity (Figure 5b). Due to packing effects the assembly deviates slightly from ideal D_{4h} symmetry, with the opposing Pd...Pd distances measuring 17.44 and 16.73 Å, respectively.

Heteroleptic Assembly of Cage C3. For the target $[\text{Pd}_2\text{L}_2^{\text{A}}\text{L}_2^{\text{B}}]^{4+}$ heteroleptic assembly, molecular modeling suggested that the geometric constraints imposed by the metal and ligand components should behave synergistically to yield only one cage isomer. DFT calculations indicated that compared to the *trans*- $[\text{Pd}_2\text{L}_2^{\text{A}}\text{L}_2^{\text{B}}]^{4+}$ cage (+131.8 kJ/mol) the formation of the *cis*- $[\text{Pd}_2\text{L}_2^{\text{A}}\text{L}_2^{\text{B}}]^{4+}$ cage from its components is significantly more energetically favorable (−65.6 kJ/mol) due to the complementary arrangement of the ligands with respect to the Pd(II) coordination sphere. In addition, cages obeying the stoichiometries $[\text{Pd}_2\text{L}_3^{\text{A}}\text{L}_1^{\text{B}}]^{4+}$ and $[\text{Pd}_2\text{L}_1^{\text{A}}\text{L}_3^{\text{B}}]^{4+}$ were found to be higher in energy than the *cis*-isomer (Figure 3). Therefore, we expected that the square planar geometry of Pd(II) and the respective backbone angles of L^{A} and L^{B} should strongly favor a *cis* arrangement of the ligands.

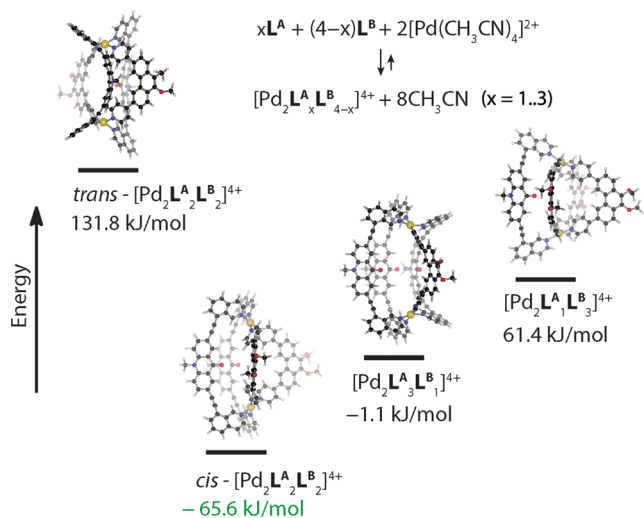


Figure 3. Energy diagram with DFT calculated structures of *trans*- $[\text{Pd}_2\text{L}_2^{\text{A}}\text{L}_2^{\text{B}}]^{4+}$, *cis*- $[\text{Pd}_2\text{L}_2^{\text{A}}\text{L}_2^{\text{B}}]^{4+}$, $[\text{Pd}_2\text{L}_3^{\text{A}}\text{L}_1^{\text{B}}]^{4+}$, and $[\text{Pd}_2\text{L}_1^{\text{A}}\text{L}_3^{\text{B}}]^{4+}$. The energies of the respective cages were calculated according to equations described in the Supporting Information. To simplify the calculations, the hexyl chain of the acridone moiety of L^{A} was replaced with a methyl substituent.

Indeed, heating a mixture of L^{A} , L^{B} , and $[\text{Pd}(\text{CH}_3\text{CN})_4]-(\text{BF}_4)_2$ in a 1:1:1 ratio for 2 h at 70 °C gave rise to a single species with a distinct ^1H NMR spectrum (Figure 2c). Interestingly, the isoquinoline protons of L^{A} , H_i and H_h , were significantly broadened in the room temperature NMR spectra. Therefore, we performed variable temperature ^1H NMR experiments (Figure S16), which revealed a gradual sharpening of all signals including the isoquinoline protons. We then performed a ^1H – ^1H COSY experiment at 70 °C, which allowed

complete assignment of the expected set of 14 aromatic proton signals for the heteroleptic $[\text{Pd}_2\text{L}_2^{\text{A}}\text{L}_2^{\text{B}}]^{4+}$ (**C3**) species (Figure S18).

In addition, we performed a NOESY experiment at 70 °C in order to assign the important interligand contacts in **C3** (Figure 4b, Figure S19). Analysis revealed several evident cross-peaks,

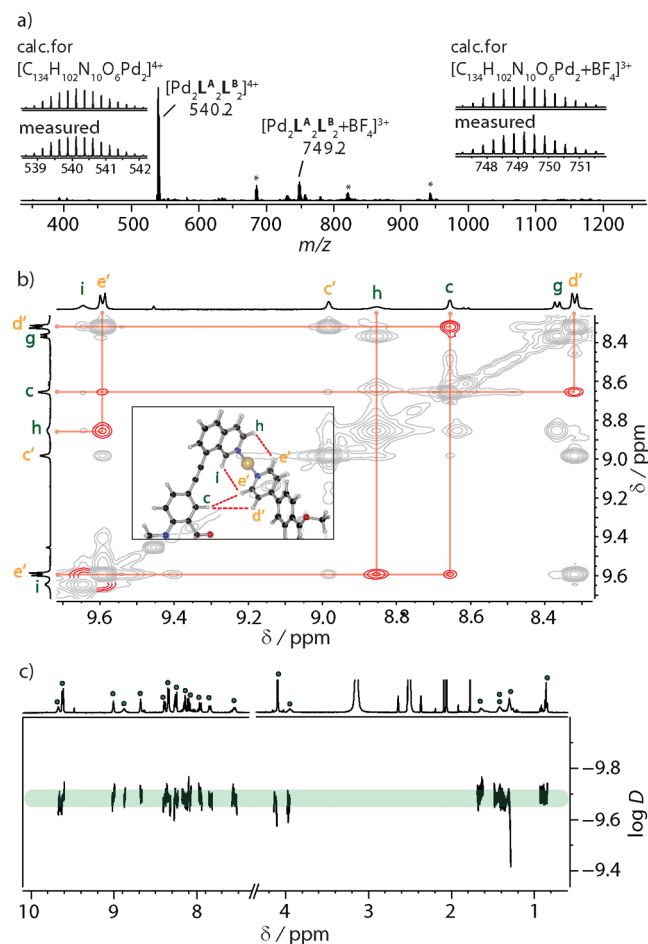


Figure 4. (a) ESI mass spectrum of $[\text{Pd}_2\text{L}_2^{\text{A}}\text{L}_2^{\text{B}} + n\text{BF}_4]^{4-n+}$ with $n = 0, 1$ ($* = [\text{Pd}_2\text{L}_3^{\text{A}}\text{L}_1^{\text{B}} + n\text{BF}_4]^{4-n+}$ with $n = 0-2$). (b) An expansion of the ^1H – ^1H NOESY spectrum of **C3** measured at 70 °C. The interligand cross peaks are highlighted in red and indicated on the DFT model of **C3** in the inset. (c) DOSY spectrum (500 MHz/DMSO, 70 °C) of **C3**. All of the signals assigned to **C3** (marked with a circle) correspond to the same diffusion coefficient ($2.14 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $\log D = -9.67$).

particularly between the isoquinoline and acridone protons of L^{A} and the pyridyl protons of L^{B} . Importantly, the observed contacts were in full agreement with the calculated model. DOSY analysis confirmed that all of the proton signals assigned to **C3** correspond to the same diffusion coefficient (Figure 4c). Further characterization of the sample by ESI HR-MS yielded a relatively simple spectrum, with the prominent signals assigned to the $[\text{Pd}_2\text{L}_2^{\text{A}}\text{L}_2^{\text{B}} + n\text{BF}_4]^{4-n+}$ species ($n = 0, 1$) (Figure 4a).

Cage-to-Cage Transformation of C1 and C2 To Give C3. Given the rapid and facile assembly of **C3** from L^{A} , L^{B} , and Pd(II), we next performed experiments to investigate whether **C3** is the thermodynamic minimum of a mixture of **C1** and **C2**. In contrast to the assembly from the individual ligands, mixing **C1** and **C2** in a 2:1 ratio resulted in a rather slow conversion to the heteroleptic species **C3**, complete after 12 days of heating at

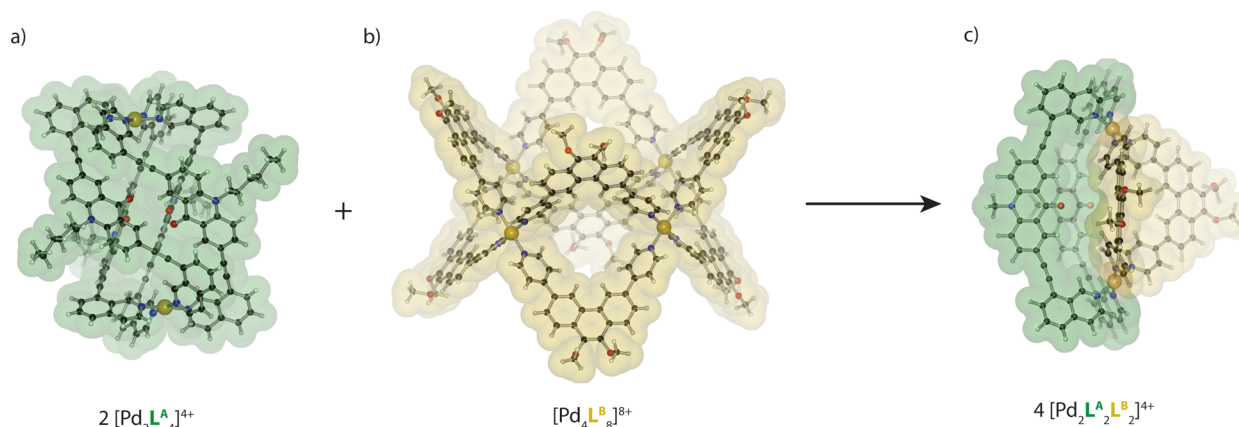


Figure 5. A perspective view of the X-ray crystal structures of (a) C1 and (b) C2 with counterions removed for clarity. (c) DFT calculated model of C3. The hexyl chain of C3 was omitted to simplify calculations. The space filling representation is overlaid for each structure (supplementary crystallographic data is found in the [Supporting Information](#) and CCDC data sets 1472456 and 1489224–1489226). The molar ratios of C1–C3 associated with the cage-to-cage transformation are included below each structure. The associated energy benefit as roughly estimated by DFT calculations is discussed in the [Supporting Information](#) (Figure S31).

70 °C (Figure S20), presumably due to the requirement of disassembling multiple coordination bonds.²² We also investigated the conversion to C3 by addition of the either L^A or L^B to C2 or C1, respectively. We observed that upon addition of L^B to C1, C3 was formed immediately at room temperature (Figure S21). Conversely, upon addition of L^A to C2, the system reached equilibrium after 2 days of heating at 70 °C with only 10% C3 formed (Figure S22). We assume differing strain within these species to be responsible for this effect. For the helical structure of C1, addition of L^B provides an opportunity to release strain via disassembly and reassembly to C3, while the same energy benefit is presumably not provided for the less strained structure of C2.

Despite numerous attempts, we were not able to obtain single crystals of C3 suitable for X-ray analysis. To obtain further insight into the assembly of C3 and investigate the observed intramolecular self-sorting, we further compared the DFT structures of C1, C2, and C3 (Figures S31 and 5c) revealing that the cage-to-cage transformation of C1 and C2 to C3 should be highly energetically favored (Figure 5 and the SI). This result supports C3 as the thermodynamic minimum of the system.

Shape Complementary Guest Binding. It is interesting to note that C3 is the first example of a [Pd₂L₄] coordination cage with a bent architecture. Because the Pd(II) metal centers can serve as anchors for charged molecules,²¹ we identified that such host architecture may possess a shape specific cavity for guest binding. To test this hypothesis, we performed ¹H NMR titrations with a straight and bent-shaped guest, 2,7-naphthalene disulfonate (G¹) and the 2,6 analogue (G²). In both cases, fast exchange was observed relative to the time scale of the experiment (Figure S23 and S24). We determined the host to guest stoichiometry to be 1:1 by the Job plot method (Figure S26) and further verified this by mass spectrometry (Figure S29 and S30). Furthermore, contacts observed in the NOESY analysis of G¹@C3 (Figure S25) revealed that the disulfonate guest is situated between the acridone backbones of the two adjacent L^A ligands in C3, most likely stabilized by π -stacking. Therefore, from the ¹H NMR titrations (Figure 6a), we calculated the association constant between G¹ and C3 and G² and C3 to be approximately 5200 and 2300 M⁻¹, respectively. This difference can be explained by the shape-complementary

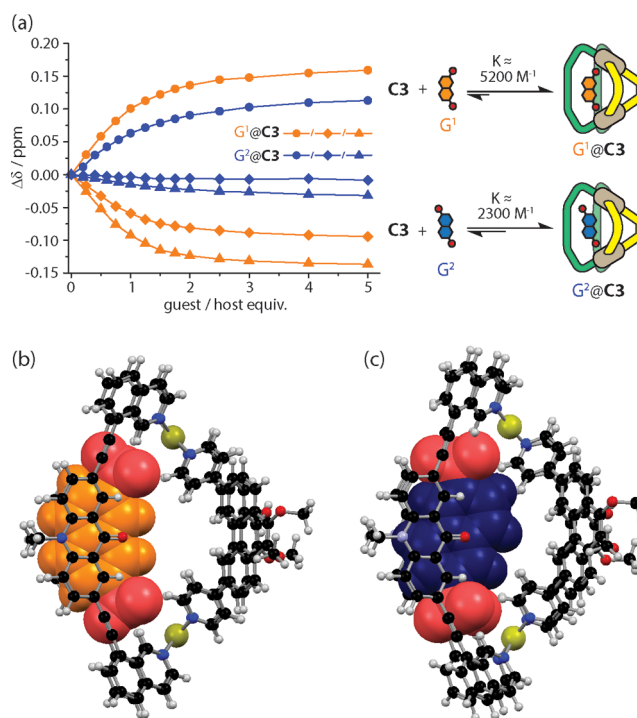


Figure 6. ¹H NMR titrations of C3 with G¹ and G². Circles, diamonds, and triangles represent the shift of protons H_e, H_c (L^B), and H_c (L^A), respectively. Panels c and d show the energy minimized structure of G¹@C3 and G²@C3, respectively.

fit of G¹ relative to the cavity and angular Pd(II) anchors of C3. To support these observations, we calculated the structures of G¹@C3 and G²@C3 (Figure 6b,c). A comparison of the minimized energies revealed that G¹@C3 is stabilized by 40.7 kJ/mol as compared to isomeric complex G²@C3, which is in accordance with the optimal fit of G¹ inside the shape-specific cavity of C3. Interestingly, previous binding studies of G¹ and G² in a [Pd₂L₄]⁴⁺ cage²³ with relationally parallel Pd(II) planes showed a stronger binding for G². Thus, the unusual cavity and angular Pd(II) anchors of C3 create a shape-specific environment with opposite guest binding preference than the previously studied example.

CONCLUSIONS

In conclusion, we have presented the self-assembly of two complementary ligands, L^A and L^B , in homoleptic and heteroleptic Pd-mediated coordination cages. We have shown that geometric complementarity preprogrammed into ligand components is a robust strategy to achieve a stable heteroleptic $cis-[Pd_2L^A_2L^B_2]^{4+}$ cage, thus surmounting the entropic tendency to form a mixture of products. Furthermore, we demonstrated that the heteroleptic architecture can be accessed through multiple self-assembly pathways: direct combination of the ligands with Pd(II), cage-to-cage transformations, and ligand induced cage rearrangements. The latter was found to proceed smoothly only in the case of addition of L^B to C1, revealing the possible strain in the C1 helical species as the driving force for this reaction. The cage-to-cage transformations also highlighted an important feature of our system; the thermodynamic stability of the heteroleptic product, allowing us to probe the cavity of C3. The unique shape of C3 and angular Pd(II) anchors indeed provided an accessible cavity, which we exploited in the shape recognition on the level of host-guest binding. We think that the implementation of this strategy into the area of $[Pd_2L_4]$ cages may yield new and unique host systems with a greater control over the incorporation of multiple functionalities and hence fine-tuning of the chemistry of the cavity. Current investigations into functionalizing the individual backbones with complementary entities (e.g., electron-donor-acceptor system) are underway in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b08694.

Experimental details and further X-ray, NMR, MS, and computational data (PDF)

Crystallographic structure of $G^1@C2$ (CIF)

Crystallographic structure of L^A (CIF)

Crystallographic structure of L^B (CIF)

Crystallographic structure of C1 (CIF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Dr. H. Frauendorf (Göttingen) for measuring the ESI mass spectra and Dr. M. John (Gö.) and Prof. Dr. W. Hiller (TU Dortmund) for assistance with NMR measurements and helpful discussions. W.M.B. thanks the Alexander von Humboldt Foundation for a postdoctoral fellowship. Y.A. thanks the Japan Society for the Promotion of Science for a fellowship. The Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft (CL 489/2-1) kindly provided financial support. We thank the European Research Council for supporting our further studies in this direction by ERC Consolidator Grant 683083 (RAMSES).

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