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Topological prediction of palladium coordination cages†

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The preparation of functionalized, heteroleptic PdLx2 coordination cages is desirable for catalytic and optoelectronic applications. Current rational design of these cages uses the angle between metal-binding (∠B) sites of the dipyridylarene linker to predict the topology of homoleptic cages obtained via non-covalent chemistry. However, this model neglects the contributions of steric bulk between the pyridyl residues—a prerequisite for endohedrally functionalized cages, and fails to rationalize heteroleptic cages. We describe a classical mechanics (CM) approach to predict the topological outcomes of PdLx2 coordination cage formation with arbitrary linker combinations, accounting for the electronic effects of coordination and steric effects of linker structure. Initial validation of our CM method with reported homoleptic Pdl24Fu24 †Fu = 2,5-bis(pyridyl)furan) assembly suggested the formation of a minor topology Pdl24Fu24 identified experimentally by mass spectrometry. Application to heteroleptic cage systems employing mixtures of †Fu (∠B = 127°) and its thiophene congener †Th (∠B = 149°) enabled prediction of Pdl24L24 and Pdl24L48 coordination cages formation, reliably emulating experimental data. Finally, the topological outcome for exohedrally †(Ex) and endohedrally †(En) functionalized heteroleptic PdLx2 coordination cages were predicted to assess the effect of steric bulk on both topological outcomes and coordination cage yields, with comparisons drawn to experimental data.

Introduction

Spherical coordination cages of type PdLx2 are formed by the self-assembly of palladium ions and organic bipyridine linkers in regular geometric patterns. The dynamic nature of Pd–pyridyl coordination has enabled the isolation of PdLx2 assemblies featuring 2–60 metal centers, isolated as the thermodynamic minima of possible structures. The internal and external surfaces can be independently functionalized to modulate the sphere environment at the nanoscale for applications. Previous reports detail a range of novel properties for guest binding, facilitating chemical reactions, modifying catalytic processes, electrochemistry, and optoelectronic applications. These useful properties are derived from the topology of the assembly, creating a significant interest in predicting topological results of self-assembly processes that ultimately lead to production of uniform assemblies of singular topology. Previously, Hay and Young described a model to predict the topology of coordination assemblies based on geometric properties of the metal center and organic linker. This model was adapted by Fujita and coworkers, using the bend angle (∠B) of the bipyridine linker to predict the topology of the thermodynamic product, applying it to describe spherical cages containing 3–60 metal centers as a principle for rational design. While this approach is sufficient for most homoleptic cages, the model fails to describe assemblies derived from asymmetric, flexible or sterically demanding linkers. This shortcoming is apparent in modern efforts to design heteroleptic cages that feature multiple functional groups to control the assembly outcome in a trial-and-error manner, especially when asymmetric linkers steric bulk or shape-complementarity are employed. The latter strategy, employed by Clever and colleagues, is especially promising for the design of small M2L4 cages with divergent functionalities. A more robust model would provide a better basis of rational design for these new structures, and the application of shape-complementarity to larger designs, motivating the aim of our research. The process of self-assembly leads to formation of supramolecular structures with the most thermodynamically stable topology, and a means to identify this product computationally would allow prediction of topologies prior to the experimental identification. While previous efforts have used computational methods to simulate the formation process, and determine the guest binding properties of cages, there is no available method for in silico screening to identify the preferred topology produced from an arbitrary linker, or set of linkers. Such a method would have practical applications as a tool for the rational design of highly functionalized cage assemblies, and furthermore provide further insight into...
known assemblies. Distinguishing the true thermodynamic products from trapped states and the identification of minor products are important issues in this regard. A viable method of in silico screening requires accuracy in estimating the free energy coupled with expediency to effectively guide experimental work. Given the size of the assemblies, numerous topologies and permutations of linker combinations, classical mechanics methods are well suited to practically address this task, with modern methodologies showing marked success in describing these assemblies.15–17

Here, we report a strategy that utilizes force field parameters for individual linkers from DFT structure optimization to estimate the relative free energies across 40 topologies containing 3–30 metal centers. The validity of our approach was demonstrated by a detailed study of the topological preferences of homoletic and heteroleptic assemblies derived from reported linkers. The feasibility of our method is demonstrated by the study of novel heteroleptic assemblies featuring a sterically demanding linker bearing endohedral functionalization. These topological predictions of our CM method are supported by experimental observations.

Methods

Experimental details

Linkers 1Fu, 1Th, 1Ex, and 1En were synthesized following standard procedures detailed in the ESI (Section D†).2–4 Homoleptic assemblies were formed with a total linker concentration of 10 mM and 0.55 equivalents of Pd(CH3CN)4(-BF4)2 at room temperature (1Fu and 1Th) or 50 °C (1Ex and 1En) after 16 hours in CD3CN. The resulting clear solutions were filtered (0.45 μm, PTFE syringe filter), following analysis by NMR and ESI-HRMS. Details of the experimental procedures and subsequent analyses are given in the ESI (Sections E–H†).

1H NMR spectra were measured using either a Bruker DRX 500 (500 MHz) or a Bruker DRX 300 (300 MHz) at 25 °C unless otherwise noted for variable temperature experiments. DOSY NMR spectra were obtained using LED bipolar pulse gradients with a diffusion delay time of 0.1 seconds at 25 °C. Mass spectra were collected on a high-resolution time-of-flight Bruker Impact II ESI-HRMS. Detection was in positive-ion mode with a source voltage between 4 and 6 kV. Samples were prepared in CD3CN with a total linker concentration of 10 mM and a Pd(CH3CN)4(-BF4)2 concentration of 5.5 mM, and then analyzed by NMR and ESI–HRMS directly.

Computational details

CM calculations were carried out using an Amber-type force-field25 and structural annealing and optimization were completed with the GPU-enabled Amber16 software suite,28 with run parameters provided in the ESI (Section B†). CM forcefield parameters were developed directly with a model system (Fig. 1).

The optimized structure of the model system was used for charge fitting based on the RESP method employed by antechamber.29 Lennard-Jones potentials for organic atom centers were assigned by GAFF atom type,31 palladium centers were parameterized according to previous reports.22 Bond, angle and torsion terms were fit using a genetic algorithm.32 Models of the complete cages were assembled by least-squares fitting placement of the individual linkers in accordance to a template using ProFit.34

The fitting and validation data sets were obtained from trajectories generated using GFN2-xTB,25 supplemented by single point energies of each trajectory frame computed by DFT at a B3LYP/def2-TZV level of theory using Gaussian 16 rev. C.26 A complete discussion of the parameterization (Scheme S1†) and validation (Table S1†) is provided in the ESI (Section A†). While only topologies containing 3–30 metal centers are considered, this approach is readily extended to Pd3L4 based assemblies, as also discussed in the ESI (Section K†).

Results and discussion

Topological survey procedure

In this study we considered the four linkers shown in Fig. 2. 1Fu (\(\beta = 127°\)) and 1Th (\(\beta = 149°\)) have been previously reported.

Fig. 2 Structures of the bipyridyl linker molecules used in this study. Bend angles, \(\beta\), are estimated from B3LYP/def2-TZV minimized structures.
and shown to form both homoleptic and heteroleptic assemblies.\textsuperscript{24} Furthermore, as the favored topology of the heteroleptic assemblies depends on the composition of linkers in the assembly, this system offers an ideal test for method development. Linkers \textsuperscript{1}Ex and \textsuperscript{1}En are novel linkers featuring exohedral and endohedral functionalization respectively. While these two linkers possess similar bend angles, the latter is sterically strained, which may impact the topological outcome of self-assembly.

Amber type forcefield parameters were developed for the four linkers employed in this study (Fig. 2), which reproduced the relative free energies for the model complex reliable compared to semi-empirical methods (Table S1\textsuperscript{1}). These linker models were then used to construct assembly models in accordance to templated defined for polyhedra containing 3–30 vertices representing many of the known cage topologies. These structures could then be annealed (2 ns) and optimized (10 000 steps) expeditiously to produce a minimum energy structure for each topology, provided in detail in the ESI (Table S4\textsuperscript{†}). The relative energy of these structures was analyzed using a Boltzmann statistical model, with each topology considered a microstate for a given linker weighted by the number of linkers involved as depicted in Scheme 1.

A majority of Pd\textsubscript{L2x} assemblies reported are homoleptic in nature due to the ease of assembly and subsequent analysis. This simple case was used in order to validate our topological survey approach. Specially the method was validated for linkers \textsuperscript{1}Fu (\(\angle B = 127^\circ\)) and \textsuperscript{1}Th (\(\angle B = 149^\circ\)). The former has been reported to afford a single topology, Pd\textsubscript{12}\textsuperscript{1}Fu\textsubscript{4}, while the latter is recently known to form a mixture, Pd\textsubscript{24}\textsuperscript{1}Th\textsubscript{48} and Pd\textsubscript{30}\textsuperscript{1}Th\textsubscript{60}. These assemblies have been sufficiently characterized by NMR, HRMS, and crystallographic means providing clear and definite knowledge of the assembly outcomes.\textsuperscript{18,27}

Our model predicted a majority (89.1\%) presence of M\textsubscript{24}\textsubscript{L24} homoleptic assemblies using linker \textsuperscript{1}Fu, which is observed experimentally (Fig. 3). Additionally, our model predicted the presence of a minor (7.8\%) Pd\textsubscript{15}\textsubscript{L10} product. We experimentally investigated the minor Pd\textsubscript{15}\textsubscript{L10} species by reproducing assemblies based on reported protocols\textsuperscript{18} and subsequent characterization of the Pd\textsubscript{L2x} assembly distribution by DOSY NMR (Fig. S13\textsuperscript{†}) and CSI-HRMS (Fig. S14\textsuperscript{†}). DOSY NMR revealed a single species (log\textsubscript{10} \(D = -9.23\)), consistent with the presence of Pd\textsubscript{12}\textsuperscript{1}Fu\textsubscript{4} as previously reported. ESI-HRMS revealed the presence of a Pd\textsubscript{12}\textsuperscript{1}Fu\textsubscript{4} assembly (Fig. 3).

Fortuitously, the relative intensity of this minor species (9.4\% of Pd\textsubscript{12}\textsuperscript{1}Fu\textsubscript{4}) correlates well to the prediction of Pd\textsubscript{12}\textsuperscript{1}Fu\textsubscript{4} abundance (8.7\%) from our computational model, as detailed in the ESI (Table S3\textsuperscript{†}). This highlights the inability of DOSY NMR to distinguish between coexisting Pd\textsubscript{12} and Pd\textsubscript{15} species originating from significant overlap of the NMR resonances, similar size (and therefore, diffusion coefficient) and the disparity between their relative populations. We applied our method to the Pd\textsubscript{L2x} assemblies formed with linker \textsuperscript{1}Th (\(\angle B = 149^\circ\)), reported to generate larger M\textsubscript{24}\textsubscript{L48} and M\textsubscript{30}\textsubscript{L60} assemblies.\textsuperscript{27} The modelling results of the homoleptic assembly formed with linker \textsuperscript{1}Th predict the formation of assemblies with either M\textsubscript{24}\textsubscript{L48} (67.0\%) or M\textsubscript{30}\textsubscript{L60} (32.8\%) topologies, further detailed in the ESI (Table S4\textsuperscript{†}).

Initial experimental reports of these assemblies afforded only the M\textsubscript{24}\textsubscript{L48} structure which was characterized by NMR, HRMS, and crystallographic means.\textsuperscript{24} However, later work afforded a mixture which included both M\textsubscript{24}\textsubscript{L48} and M\textsubscript{30}\textsubscript{L60} topologies, the latter of which was additionally

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image1.png}
\caption{(A) ESI-HRMS characterization of the homoleptic assembly products of linker \textsuperscript{1}Fu (red), top. Mass simulations indicate multiple charged species matching simulations for Pd\textsubscript{12}\textsuperscript{1}Fu\textsubscript{4} (black), and Pd\textsubscript{15}\textsuperscript{1}Fu\textsubscript{30} (green) species. Bottom, an expanded view of the isotope distributions observed for (B) Pd\textsubscript{12}\textsuperscript{1}Fu\textsubscript{4} (BF\textsubscript{4}\textsubscript{13}⁻), and (C) Pd\textsubscript{15}\textsuperscript{1}Fu\textsubscript{30} (BF\textsubscript{4}\textsubscript{21}⁻), species, annotated with the center peak m/z either observed (red) or calculated (black or green). Data is further detailed in the ESI (Fig. S15\textsuperscript{†}).}
\end{figure}

\begin{scheme}[h]
\centering
\includegraphics[width=\textwidth]{image2.png}
\caption{Flow chart for topological prediction of homoleptic assemblies featuring the formation of homoleptic Pd\textsubscript{L2x} assemblies. The linker structure is used to construct a library of possible assembly outcomes, which are subjected to a simulated annealing and structural optimization procedure using implicit solvation. The resulting minimum energies, \(E\), are treated as microstates, and the topological distribution is determined using Boltzmann statistics with a weighting factor \(\lambda\) corresponding to the number of linker components in the assembly.}
\end{scheme}
characterized by NMR, HRMS, and crystallographic means. Our CM approach was unaffected by the kinetic differences for forming either topologies and the resulting topological distribution contain these two species at relative populations in good agreement with the experimentally reported data.

**Topological prediction of heteroleptic Pd\textsubscript{12}L\textsubscript{24x} assembly distribution**

The formation of heteroleptic assemblies is a significant motivation for topological prediction as there is no apparent rule to predict the assembly outcome for the combination of two dissimilar linkers. Therefore, we expanded our survey to consider assemblies composed of two linkers, randomly distributed over the edges of the polyhedral templates. To validate this extension, we considered the previously reported heteroleptic assemblies of \( ^{1}\text{Th} \) and \( ^{1}\text{Fu}. \)

A new approach was needed in order to identify the topological preference of mixtures of linkers at arbitrary compositions using a linear of the relative free energy for each topology at various compositions (Fig. 4). This approach is further detailed in the ESI (Section C).

Our model predicts that heteroleptic assemblies with a \( M_{12}L_{24} \) topology are produced from mixtures of \( ^{1}\text{Fu} \) and \( ^{1}\text{Th} \) containing less than 27% of \( ^{1}\text{Th} \). At this critical concentration a transition in topological preference is observed, shifting towards the \( M_{24}L_{18} \) topology. This critical composition is in agreement with the previous report observing the transition occurring at 0.2–0.3 mole fraction \( ^{1}\text{Th}. \) The model predicts greater preference for the \( M_{15}L_{30} \) topology at this critical point, suggesting it may be an important intermediate between the two topologies.

**The effect of endohedral functionalization on topological distribution**

Moving beyond the bend angle, we used our model to study the topological effect of endohedral and exohedral substituents. Linker \( ^{1}\text{Ex} \) features external ornamentation that should impart minimal effect on \( \text{Pd}_{12}\text{L}_{xx} \) assembly topology, as homoletic assemblies of similar linkers have been reported to form \( M_{12}\text{L}_{24} \) topologies. Linker \( ^{1}\text{En} \), with internal functionalization demonstrate the same apparent bend angle as \( ^{1}\text{Ex} \) suggesting the same topology should form. However, reports of a similar linker featuring a methoxy substituent by Fujita et al., concluded that \( \text{Pd}_{12}\text{L}_{xx} \) assembly formation is inhibited assemblies due to the sterical encumbrance imparted by substituents in this position. To maximize this steric effect, a benzyl group was selected in the design of linker \( ^{4}\text{En}. \)

Shown in Fig. 5, our topological prediction shows the \( M_{12}\text{L}_{24} \) topologies are favored over a large range of compositions, as would be suggested by the bend angle. Interestingly, at mixtures containing a larger proportion of \( ^{1}\text{En} \), the formation of larger topologies (\( i.e. M_{24}L_{18} \) or \( M_{30}L_{60} \)) are favored. As the \( ^{1}\text{En} \) bend angle (\( \angle B = 124^\circ \)) favors \( M_{12}\text{L}_{24} \) topologies, the preference towards larger assemblies can only be ascribed to the effect of the sterical bulk.

As expected, homoletic assemblies were successfully formed with \( ^{1}\text{Ex} \), evidenced by the characteristic shift of \( \alpha \)-pyridyl proton resonances in \( ^{1}\text{H} \) NMR. Subsequent characterization of the assembly by DOSY NMR revealed a hydrodynamic radius of 16.4 Å, identical to the radius found for the \( \text{Pd}_{12}\text{L}_{24} \) model (Table S4†). Finally, isotope pattern analysis within the ESI-MS data enabled for unambiguous assignment of \( \text{Pd}_{12}\text{L}_{24} \) cage topologies (Fig. S19†).

Similarly, homoletic assemblies of \( ^{1}\text{En} \) were successfully formed on the basis of the characteristic downfield shift of \( \alpha \)-pyridyl proton resonances, and the absence of free building block in \( ^{1}\text{H} \) NMR. However, DOSY NMR indicated that resulting assemblies possess a radius of 27.8 Å (Fig. S22†). While this value is significantly larger than the 17.6 Å predicted by our
model of Pd_{12}^{1}En_{24} cages, it is a reasonable radius for Pd_{60}^{1}En_{60} assemblies. Unfortunately, the difficulty in reliably ionizing this species meant that its presence could not be confirmed by ESI-HRMS, thus the composition of the assembly (or assemblies) formed experimentally remains ambiguous. These limitations of ESI-HRMS are known for the analysis of larger assemblies, experimentally limiting the pursuit of these structures.  

Heteroleptic assemblies were formed using five different ratios of ^{1}Ex : ^{1}En linkers, incorporating 4–20 of ^{1}En (mole fractions 0.14–0.86) and 20–4 ^{1}Ex (Fig. 6). The formation of these assemblies was confirmed by the characteristic downfield shift of the \( \alpha \)-pyridyl proton (ca. 9.05 to 9.25 ppm). DOSY NMR indicated that the resulting assemblies were larger than expected for M_{24}L_{48} topologies \((r_{H} 18–21 \text{ Å})\), but within expectations for M_{24}L_{48} or M_{30}L_{60} topologies \((r_{H} 23–26 \text{ Å})\). These data are provided in the ESI (Section H†). It is well documented that intermediate polymeric species present during assembly formation are NMR silent,^{28,29} and therefore can be excluded as a major product. 

Mass analysis of the heteroleptic assemblies were found to include 0–21 ^{1}En randomly incorporated into the assembly structure with an average ratio corresponding to the composition of the reaction mixture, summarized by Fig. 6. Mass analysis yielded only compositions with a stoichiometry of Pd_{12}^{1}En_{12}^{1}Ex_{(24–x)} corresponding only to the Pd_{12}L_{24} topologies. This contradicts the DOSY NMR results indicating the formation of larger species containing 24–30 metal centers. Interestingly the overall intensity of the mass signal decreases with the increase in ^{1}En content. If this decrease were due to simple differences in assembly formation, ionizability, or instrument response, a bias should be observed in the distributions of Pd_{12}^{1}En_{12}^{1}Ex_{(24–x)} species formed. Alternatively, this diminished intensity can be attributed to the presence of a secondary species—plausibly Pd_{24}^{1}En_{4}^{1}Ex_{(48–x)} or Pd_{30}^{1}En_{6}^{1}Ex_{(60–x)} cages—which are beyond the current limits of this particular ESI-HRMS analytical technique and therefore cannot be conclusively characterized. 

**Impaired dihedral rotation and long-range topological effects**

From the above data we surmise that heteroleptic assemblies of ^{1}En and ^{1}Ex form under conditions similar to other palladium-pyridyl coordination cages. Furthermore, these cages possess a larger topology due to the steric effects of the endohedral functionalization of ^{1}En. To understand the mechanism of this steric effect and its impact on topological preferences for heteroleptic assemblies, relaxed potential energy surfaces were computed for the pyridyl-arene dihedral rotation using DFT at a B3LYP/def2-TZV theory level as illustrated in Fig. 7. While relaxed scans were used, the method converges to local minima resulting in the distinct AA and \( \Delta \Delta \) atropisomers shown in Fig. 8A. These potential energy surfaces reveal that the pyridyl-arene dihedral rotations for the sterically demanding ^{1}En are asymmetric compared to ^{1}Ex. The structures generated from this scan were analyzed using our CM parameters, producing similar results as shown in the ESI (Section J†).

The DFT potential energy surface shows that AA or \( \Delta \Delta \) isomers of ^{1}En are less favorable by 2.2 kcal mol^{−1}. The preference for the AA atropoisomer is easily rationalized by the minimization of steric interactions between the pyridyl groups and the endohedral benzyl functionality. Similarly, the high
energy ΔΔ isomer forces the pyridyl groups to rotate into the endohedral benzyl functionality, and therefore such conformation is not physically accessible.

Reproduction of these dihedral scans using our CM method produces similar minima with ΔΔ or ΔΔ isomers being only 1.2 kcal mol$^{-1}$ higher in energy, as discussed in detail in the ESI (Section J†). Contrary to the computed preference of the ΔΔ isomer, our CM models of assemblies feature predominantly ΔΔ or ΔΔ isomers shown in Fig. 8.

We speculate that this arrangement is a requirement for coordination to satisfy coordination and results in a destabilization of cages proportional to the number of triangular faces involved. This aggregate effect was modeled directly using our CM approach to consider specific arrangements of linkers for Pd$_{12}^{1}{\text{En}}^{n}^{2}{\text{Ex}}^{20}$ assemblies following the same annealing and optimization methodology used for previously. The relative free energies were computed for four different distributions representative of the intuitive outcomes for different degrees of interaction between $^{1}$En linkers.

Based on our model, the non-interacting arrangement (Fig. 9A) is significantly more favorable than co-coordinated or co-facial arrangements (Fig. 9B–D). However, the possibility of forming these favorable arrangements becomes insignificant with increasing $^{1}$En content, necessitating the more accessible co-facial arrangements. The relative free energy of co-facial $^{1}$En on a triangular face (Fig. 9D) were less favored compared to the co-facial square (Fig. 9C) arrangements by 1.8 kcal mol$^{-1}$ per linker. In turn this accounts for the observation that assemblies of $^{1}$En form larger topologies (i.e. M$_{42}$L$_{24}$ and M$_{50}$L$_{60}$) as they feature a smaller proportion of triangular faces (8/26 and 8/38 faces, respectively) compared to M$_{12}$L$_{24}$ (8/14 faces) topologies. Similarly, the incorporation of the more adaptable $^{1}$Ex alleviates permits the formation of spherical cages with a smaller M$_{12}$L$_{24}$ topology that would otherwise be favored by the natural bend angle of both linkers.

These computational results account for the experimental observations of heteroleptic assemblies for $^{1}$Ex and $^{1}$En, where DOSY NMR shows the formation of a larger complex, and the mass spectra results which present an unexpected loss of intensity. While it is unfortunate that available experimental methods cannot fully characterize and quantitatively assess these larger species, our CM model provides deeper insights into these assemblies and is well supported by both higher-level calculations and available experimental evidence.

**Conclusions**

In this work we produced a forcefield for pyridyl-palladium complexes as found in a number of coordination assemblies. This forcefield offers significant improvements to accurately estimates of relative free energies of palladium–pyridyl complexes. Using these estimates, we could predict the topological preferences of two previously reported bis-pyridyl linkers, $^{1}$Th and $^{1}$Fu, reproducing experimentally observed topological preferences for their homoleptic and heteroleptic assemblies. From our results we found a novel minority M$_{15}$L$_{30}$ topology which we characterized experimentally. These outcomes demonstrate the viability of a classical mechanics based in silico screening for these topological outcomes.

This approach was then used to determine the topological outcome of heteroleptic assemblies formed from two novel linkers, $^{1}$Ex and $^{1}$En, respectively featuring exohedral and endohedral functionalization. This study demonstrated the pronounced effect of steric bulk proximal to metal binding sites in topological outcomes and assembly yields, as confirmed by
experimental study with high resolution mass spectrometry. These heteroleptic assemblies demonstrate a novel strategy for the inclusion of sterically demanding functionalization within coordination cages, and highlight the effectiveness of our classical mechanics methodology to aid in assembly design.

Future work aims to apply these computational approaches to provide more detailed insight in the formation of these self-assembled nanospheres, and to extend these approaches to include to better suit the analysis of applied supramolecular structures.

Conflicts of interest

There are no conflicts to declare.

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