

## Supramolecular Chemistry

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# LiBF<sub>4</sub>-Induced Rearrangement and Desymmetrization of a Palladium-Ligand Assembly

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**Abstract:** Thirteen palladium-ligand assemblies with different structures and topologies were investigated for the ability to bind lithium ions. In one case, the addition of LiBF<sub>4</sub> resulted in a profound structural rearrangement, converting a dinuclear [Pd<sub>2</sub>L<sub>4</sub>]<sup>4+</sup> complex into a low-symmetry [Pd<sub>4</sub>L<sub>8</sub>]<sup>8+</sup> assembly with two binding pockets for solvated LiBF<sub>4</sub> ion pairs. The rearrangement could only be induced by Li<sup>+</sup>, indicating highly specific host-guest interactions. A structural analysis of the [Pd<sub>4</sub>L<sub>8</sub>]<sup>8+</sup> receptor revealed a compact structure with multiple intramolecular interactions, reminiscent of what is seen for natural and synthetic foldamers.

The host-guest chemistry of palladium-based assemblies has been investigated extensively,<sup>[1]</sup> and these studies have led to applications in medicinal chemistry<sup>[2]</sup> and catalysis.<sup>[3]</sup> The majority of the known guest molecules are either anionic<sup>[4]</sup> or neutral,<sup>[5]</sup> and dominant factors for guest binding are electrostatic forces and solvophobic interactions. Cations appear to be less suited as guests for Pd<sup>II</sup>-based hosts, because the hosts themselves are polycationic species. However, it was found that charge-charge repulsions are not necessarily prohibitive for encapsulation of cationic guests. One possibility for diminishing detrimental Pd<sup>2+</sup>-[guest]<sup>n+</sup> interactions is the co-complexation of anions, which act as an “electrostatic glue”.<sup>[6]</sup> Other options are the functionalization of the host with cation-binding groups,<sup>[7]</sup> or charge compensation by the ligand.<sup>[8]</sup>

We have recently observed the complexation of Na<sup>+</sup> ions inside a tetrahedral [Pd<sub>4</sub>L<sub>8</sub>]<sup>8+</sup> cage.<sup>[6a]</sup> The binding was enabled by co-encapsulation of four BF<sub>4</sub><sup>-</sup> anions. Intrigued

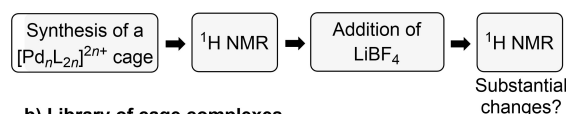
by the finding that a simple Na<sup>+</sup> ion can be bound inside a [Pd<sub>4</sub>L<sub>8</sub>]<sup>8+</sup> cage, we have examined if other [Pd<sub>n</sub>L<sub>2n</sub>]<sup>2n+</sup> cages would also be able to bind alkali metal ions. In particular, we were interested if they could bind lithium ions. Li<sup>+</sup> is a challenging guest due to its high solvation energy.

For our investigations, we have prepared 13 different [Pd<sub>n</sub>L<sub>2n</sub>]<sup>2n+</sup> complexes (as BF<sub>4</sub><sup>-</sup> salts), all of which had been described in the literature (Figure 1). The small library contained diverse architectures including simple dinuclear [Pd<sub>2</sub>L<sub>4</sub>]<sup>4+</sup> complexes, a macrocyclic [Pd<sub>3</sub>L<sub>6</sub>]<sup>6+</sup> complex, cages ([Pd<sub>4</sub>L<sub>8</sub>]<sup>8+</sup>, [Pd<sub>6</sub>L<sub>12</sub>]<sup>12+</sup>, [Pd<sub>12</sub>L<sub>24</sub>]<sup>24+</sup>), heteroleptic complexes ([Pd<sub>2</sub>L<sub>2</sub>L'<sub>2</sub>]<sup>4+</sup> and [Pd<sub>6</sub>L<sub>6</sub>L'<sub>6</sub>]<sup>12+</sup>), and an interlocked [Pd<sub>4</sub>L<sub>8</sub>]<sup>8+</sup> species (for details, see the Supporting Information).

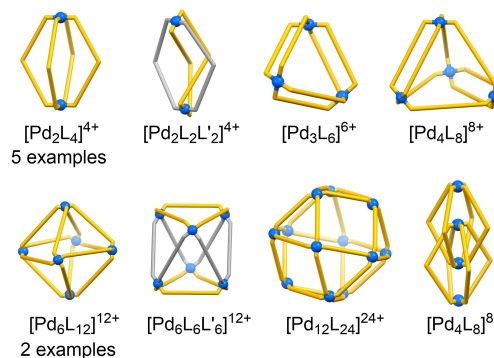
The synthesis of the 13 complexes was accomplished by mixing [Pd(CH<sub>3</sub>CN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> with the corresponding ditopic N-donor ligand(s) in CD<sub>3</sub>CN and tempering for 12 h at 70 °C. The success of the self-assembly process was verified by <sup>1</sup>H NMR spectroscopy. Subsequently, LiBF<sub>4</sub> (50 equiv) was added and another <sup>1</sup>H NMR spectrum was recorded. A potential interaction with LiBF<sub>4</sub> was evaluated by comparing the spectra before and after addition of the salt. (see the Supporting Information, Figures S3–S15). The screening of 13 potential hosts gave two “hits”.

For a tetranuclear Pd complex based on ligand **L1** (Scheme 1),<sup>[9]</sup> the addition of LiBF<sub>4</sub> (50 equiv) resulted in

## a) Screening procedure



## b) Library of cage complexes

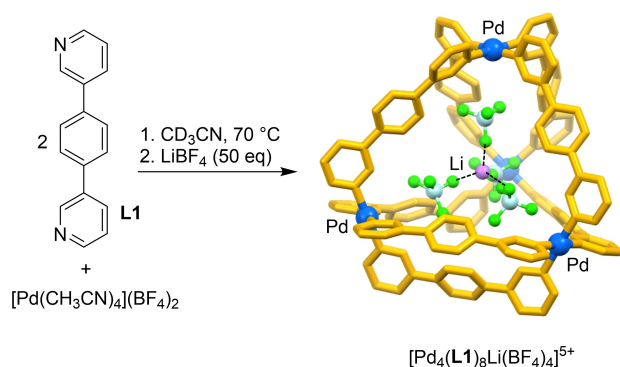


**Figure 1.** NMR-based screening for interaction of LiBF<sub>4</sub> with [Pd<sub>n</sub>L<sub>2n</sub>]<sup>2n+</sup> assemblies (BF<sub>4</sub><sup>-</sup> salts).

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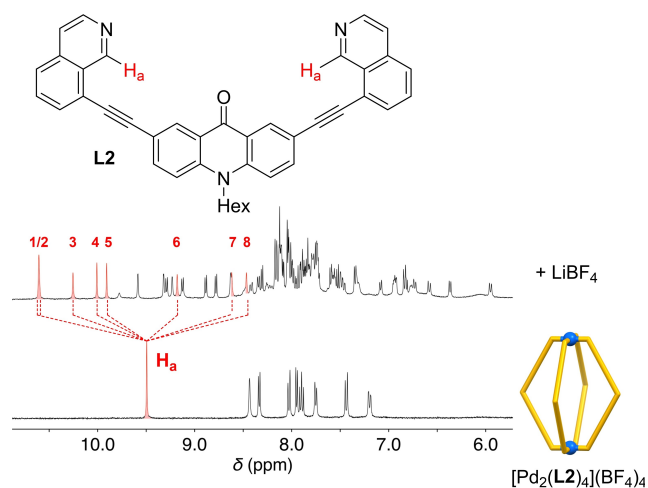
**Scheme 1.** Encapsulation of  $[\text{Li}(\text{BF}_4)_4]^{3-}$  by the tetranuclear complex  $[\text{Pd}_4(\text{L1})_8]^{8+}$ . The structure of the host-guest complex is based on a crystallographic analysis. Hydrogen atoms are not shown for clarity. Color coding: Pd: blue, C and N: yellow, F: green, B: light cyan.

shifts in the NMR spectrum of up to 0.1 ppm (Supporting Information, Figure S3). A more elaborate NMR titration experiment was performed using a variable amount of  $\text{LiBF}_4$  (10–200 equiv, Supporting Information, Figure S16). The resulting isotherm was fitted to a 1:1 binding model yielding an apparent binding constant of  $K_a = 26(\pm 2) \text{ M}^{-1}$  (Supporting Information, Figures S17).<sup>[10]</sup>  $\text{Li}^+$  complexation could be corroborated by a crystallographic analysis.<sup>[11]</sup> The structural data show that binding of the cation is achieved by co-encapsulation of four  $\text{BF}_4^-$  anions, which are situated in-between the  $\text{Pd}^{2+}$  ions and the  $\text{Li}^+$  ion. (Scheme 1). The larger  $\text{Na}^+$  could be encapsulated in a similar fashion, as evidenced by a crystallographic analysis of the host-guest complex (Supporting Information, Figure S35).<sup>[11]</sup> A quantification of  $\text{Na}^+$  binding was hampered by the low solubility of  $\text{NaBF}_4$  in acetonitrile, which prevented NMR titration experiments.

The second “hit” in our screening was a dinuclear cage based on ligand **L2**.<sup>[12]</sup> Directly after addition of  $\text{LiBF}_4$ , we observed complexation-induced chemical shifts. However, the NMR spectrum changed with time, indicating the formation of a new complex. The rearrangement occurred with a half-life of 135 min, and it was complete within 20 hours (Supporting Information, Figures S4, S29).<sup>[13,14]</sup> Subsequent analysis by mass spectrometry revealed the formation of a  $[\text{Pd}_4\text{L}_8]^{8+}$  assembly (Supporting Information, Figures S27, S28). The tetranuclear complex could also be obtained by equilibrating a mixture of  $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ , **L2**, and  $\text{LiBF}_4$  in a 1:2:15 ratio at 70 °C for 12 h (Supporting Information, Figure S18).

A striking feature of the new complex was its low apparent symmetry: the  $^1\text{H}$  NMR signals of the aromatic CH protons were found to split eight times (Figure 2). This splitting was evidenced by analysis of the  $^{13}\text{C}$  and  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectra (Supporting Information, Figures S19, S20, S22, and S23). Surprisingly, the splitting observed in the NMR spectra did not match with any of the known topologies for  $[\text{Pd}_4\text{L}_8]^{8+}$  assemblies, namely: macrocyclic,<sup>[15]</sup> distorted tetrahedral,<sup>[6a,9,16]</sup> and interlocked.<sup>[5h,17]</sup>

The rearrangement was only observed for lithium salts ( $\text{LiBF}_4$  or  $\text{LiOTf}$ ). The addition of  $\text{NaOTf}$  or  $\text{KPF}_6$  to a



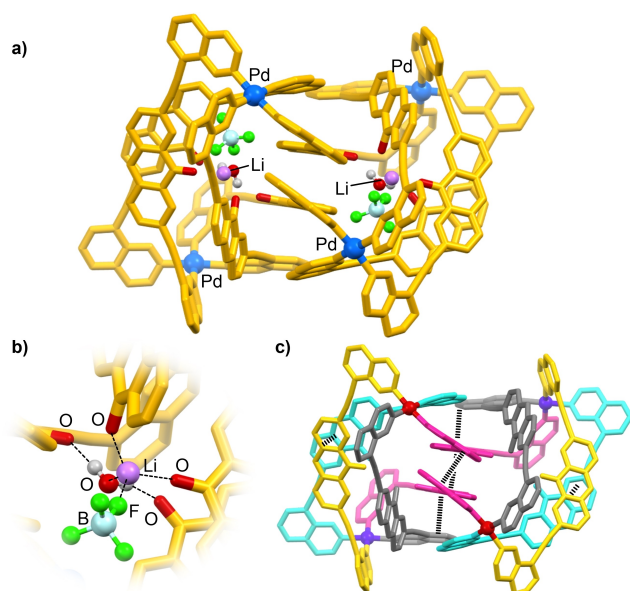
**Figure 2.** Part of the  $^1\text{H}$  NMR spectra of a mixture of  $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$  (1 equiv) and **L2** (2 equiv) after tempering at 70 °C for 12 h in the absence (bottom) or in the presence of  $\text{LiBF}_4$  (15 equiv, top).

solution of  $[\text{Pd}_2(\text{L2})_4](\text{BF}_4)_4$  in  $\text{CD}_3\text{CN}$  resulted in broadening of the ligand signals, but a new species could not be detected. For  $\text{CsBPh}_4$ , no change in the NMR spectra was observed at all (Supporting Information, Figure S32). Notably, the rearrangement was also observed for mixtures of  $\text{LiOTf}$  and  $\text{NaOTf}$ , indicating that the low-symmetry Pd complex has a very high selectivity for lithium over sodium salts (Supporting Information, Figure S33).<sup>[18,19]</sup>

Single crystals of the new Pd assembly were obtained by slow vapor diffusion of diethyl ether into a solution of the complex in  $\text{CD}_3\text{CN}$ .<sup>[11]</sup> The results of a crystallographic analysis showed that a tetranuclear  $[\text{Pd}_4(\text{L2})_8](\text{BF}_4)_8$  complex had formed (Figure 3a).

The assembly features two symmetry-related binding pockets (the complex has one crystallographic  $C_2$  symmetry axis).<sup>[20]</sup> Each pocket is occupied by a  $\text{LiBF}_4$  ion pair and a water molecule. The  $\text{Li}^+$  ion shows a tetrahedral coordination environment with close contacts to one  $\text{BF}_4^-$  anion ( $\text{Li}-\text{F} = 1.851(7) \text{ \AA}$ ), one water molecule ( $\text{Li}-\text{O} = 1.902(7) \text{ \AA}$ ), and two carbonyl groups of ligand ( $\text{Li}-\text{OC} = 1.895(8) \text{ \AA}$ ,  $\text{Li}-\text{O}' = 1.907(8) \text{ \AA}$ ) (Figure 3b). Two other carbonyl groups are involved in hydrogen bonding to the water molecule. The latter was found to be crucial for the re-arrangement: when heat-dried  $\text{LiBF}_4$  was added to a solution of  $[\text{Pd}_2(\text{L2})_4](\text{BF}_4)_2$  in dry  $\text{CD}_3\text{CN}$ , the formation of  $[\text{Pd}_4(\text{L2})_8](\text{BF}_4)_8$  could not be detected. Instead, only broadening of the  $^1\text{H}$  NMR signals was observed, similar as what was found for  $\text{NaOTf}$ . Quantitative conversion into  $[\text{Pd}_4(\text{L2})_8](\text{BF}_4)_8$  could then be triggered by addition of small amounts of  $\text{D}_2\text{O}$  to the solution (Supporting Information, Figure S34).

The molecular structure of  $[\text{Pd}_4(\text{L2})_8](\text{BF}_4)_8$  in the crystal is in line with the low symmetry detected by NMR spectroscopy. There are four pairs of symmetry-related ligands (Figure 3c). Since the ligands bridge chemically non-equivalent  $\text{Pd}^{2+}$  ions, the two isoquinoline donor groups are also no longer equivalent.<sup>[21]</sup> The four chemically distinct ligands and the reduced internal ligand symmetry gives rise



**Figure 3.** a) Molecular structure of  $[\text{Pd}_4(\text{L}2)_8]^{8+}$  in the crystal with two  $\text{LiBF}_4 \cdot \text{H}_2\text{O}$  guests molecules. Hydrogen atoms, most  $\text{BF}_4^-$  anions, and the hexyl side chains are not shown for clarity. Color coding: Pd: blue, O: red; C and N: yellow, F: green, B: light cyan. b) Close-up view on the binding pocket. c) Graphic representation of  $[\text{Pd}_4(\text{L}2)_8]^{8+}$  highlighting intra-ligand  $\pi$ -stacking interactions. The color coding indicates symmetry-related ligands and  $\text{Pd}^{2+}$  ions.

to the multiplicity of 8 for the  $^1\text{H}$  NMR signals of the aromatic protons (Figure 2). The  $[\text{Pd}_4(\text{L}2)_8]^{8+}$  complex adopts a very compact structure, with numerous  $\pi$ -stacking interactions between the aromatic groups of the ligands (Figure 3c). Such tight intramolecular packing is reminiscent of what is found for biopolymers and for synthetic foldamers.<sup>[22,23]</sup> It is worth pointing out that the folding of  $[\text{Pd}_4(\text{L}2)_8](\text{BF}_4)_8$  is essential for its low apparent symmetry. In terms of connectivity, the complex displays only three pairs of chemically distinct ligands (the ligands shown in Figure 3c in cyan and in grey could be interconverted by a conformational change). Attempts to unfold the assembly thermally were not successful. Even at  $70^\circ\text{C}$ , the multiplicity of the NMR signals ( $\text{CD}_3\text{CN}$ ) was not changed (Supporting Information, Figure S26).

The prevalence of  $\pi$ -stacking interactions in  $[\text{Pd}_4(\text{L}2)_8]^{8+}$  suggested that hydrophobic effects might stabilize the assembly. In order to examine if a higher solvent polarity could also lead to structures other than  $[\text{Pd}_2(\text{L}2)_4]^{4+}$ , we have carried out the reaction between  $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$  and **L2** in a mixture of  $\text{CD}_3\text{CN}$  and  $\text{D}_2\text{O}$  (9:1).<sup>[24]</sup> After equilibration for 5 days at  $70^\circ\text{C}$ , the solution was analyzed by  $^1\text{H}$  NMR spectroscopy and mass spectrometry. The  $^1\text{H}$  NMR spectrum showed several new peaks along with those of  $[\text{Pd}_2(\text{L}2)_4](\text{BF}_4)_4$  (Supporting Information, Figure S30), and the MS spectrum showed dominant peaks corresponding to a  $[\text{Pd}_2(\text{L}2)_5]^{4+}$  assembly (Supporting Information, Figure S31). Apparently, the increase in solvent polarity was not sufficient to promote formation of a larger tetranuclear assembly, but the results are further evidence that ligand **L2** facilitates formation of alternative structures.

To conclude: Pd-based assemblies were investigated for their ability to bind lithium salts. Finding two hits within a small set of thirteen potential hosts indicates that anion-mediated binding of cations is likely a more common phenomenon for poly-cationic metal-ligand assemblies. Notably, our investigations revealed that a solvated  $\text{LiBF}_4$  ion pair can induce the rearrangement of a  $[\text{Pd}_2\text{L}_4]^{4+}$  complex into a  $[\text{Pd}_4\text{L}_8]^{8+}$  assembly. The template effect is highly specific as it requires the presence of  $\text{Li}^+$ . Other alkali metal ions were not able to promote a change in structure. A unique feature of the  $[\text{Pd}_4\text{L}_8]^{8+}$  complex is its low symmetry with four chemically distinct ligand environments.<sup>[25,26]</sup> The possibility to adopt a folded, highly compact structure is a crucial factor, and ligand **L2** is well suited in that regard. It displays moderate conformational flexibility, variable coordinate vectors of the N-donor groups, and large aromatic groups, which allow for  $\pi$ -stacking interactions. In addition, the carbonyl groups can form additional interactions with a guest. It is worth drawing a comparison with folded organic macrocycles, which were recently reported by the groups of Huc and Otto.<sup>[27]</sup> Despite being obtained from only one type of building block, the macrocycles showed up to 12 chemically distinct sub-components. The authors argue that folding into low-symmetry structures requires building blocks with an intermediate flexibility, and with the possibility to engage in diverse non-covalent interactions. These criteria are fulfilled for **L2**. Current studies in our laboratory are aimed at providing more precise guidelines for the construction of homoleptic metal-ligand assemblies with folded, low-symmetry structures.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

**Keywords:** Cages · Palladium · Self-Assembly · Supramolecular Chemistry · Symmetry

- [1] a) H. Takezawa, M. Fujita, *Bull. Chem. Soc. Jpn.* **2021**, *94*, 2351–2369; b) F. J. Rizzuto, L. K. S. von Krbek, J. R. Nitschke, *Nat. Chem. Rev.* **2019**, *3*, 204–222; c) M. Yoshizawa, L. Catti, *Acc. Chem. Res.* **2019**, *52*, 2392–2404; d) S. Saha, I. Regeni, G. H. Clever, *Coord. Chem. Rev.* **2018**, *374*, 1–14; e) G. H. Clever, P. Punt, *Acc. Chem. Res.* **2017**, *50*, 2233–2243; f) M. Han, D. M. Engelhard, G. H. Clever, *Chem. Soc. Rev.* **2014**, *43*, 1848–1860; g) K. Harris, D. Fujita, M. Fujita, *Chem. Commun.* **2013**, *49*, 6703–6712; h) M. Yoshizawa, J. K. Klosterman, M. Fujita, *Angew. Chem. Int. Ed.* **2009**, *48*, 3418–3438; *Angew. Chem.* **2009**, *121*, 3470–3490.
- [2] A. Casini, B. Woods, M. Wenzel, *Inorg. Chem.* **2017**, *56*, 14715–14729.
- [3] a) Y. Xue, X. Hang, J. Ding, B. Li, R. Zhu, H. Pang, Q. Xu, *Coord. Chem. Rev.* **2021**, *430*, 213656; b) A. B. Grommet, M. Feller, R. Klajn, *Nat. Nanotechnol.* **2020**, *15*, 256–271; c) A. C. H. Jans, X. Caumes, J. N. H. Reek, *ChemCatChem* **2019**, *11*, 287–297; d) L. J. Jongkind, X. Caumes, A. P. T. Hartendorp, J. N. H. Reek, *Acc. Chem. Res.* **2018**, *51*, 2115–2128; e) I. Sinha, P. S. Mukherjee, *Inorg. Chem.* **2018**, *57*, 4205–4221.
- [4] For selected examples, see: a) A. P. Birve, H. D. Patel, J. R. Price, W. M. Bloch, T. Fallon, *Angew. Chem. Int. Ed.* **2022**, *61*, e202115468; *Angew. Chem.* **2022**, *134*, e202115468; b) H. Danjo, K. Asai, T. Tanaka, D. Ono, M. Kawahata, S. Iwatsuki, *Chem. Commun.* **2022**, *58*, 2196–2199; c) B. J. J. Timmer, T. J. Mooibroek, *Chem. Commun.* **2021**, *57*, 7184–7187; d) S. Hasegawa, S. L. Meichsner, J. J. Holstein, A. Baksi, M. Kasanmanscheff, G. H. Clever, *J. Am. Chem. Soc.* **2021**, *143*, 9718–9723; e) T. Zhang, L.-P. Zhou, X.-Q. Guo, L.-X. Cai, Q.-F. Sun, *Nat. Commun.* **2017**, *8*, 15898; f) L.-P. Zhou, Q.-F. Sun, *Chem. Commun.* **2015**, *51*, 16767–16770; g) S. Freye, J. Hey, A. Torras-Galan, D. Stalke, R. Herbst-Irmer, M. John, G. H. Clever, *Angew. Chem. Int. Ed.* **2012**, *51*, 2191–2194; *Angew. Chem.* **2012**, *124*, 2233–2237; h) G. H. Clever, S. Tashiro, M. Shionoya, *Angew. Chem. Int. Ed.* **2009**, *48*, 7010–7012; *Angew. Chem.* **2009**, *121*, 7144–7146; i) D. K. Chand, K. Biradha, M. Fujita, *Chem. Commun.* **2001**, 1652–1653.
- [5] For selected examples, see: a) X. Schaapkens, R. N. Van Sluis, E. O. Bobylev, J. N. H. Reek, T. J. Mooibroek, *Chem. Eur. J.* **2021**, *27*, 13719–13724; b) Y. Tamura, H. Takezawa, M. Fujita, *J. Am. Chem. Soc.* **2020**, *142*, 5504–5508; c) B. Chen, J. J. Holstein, S. Horiuchi, W. G. Hiller, G. H. Clever, *J. Am. Chem. Soc.* **2019**, *141*, 8907–8913; d) B. M. Schmidt, T. Osuga, T. Sawada, M. Hoshino, M. Fujita, *Angew. Chem. Int. Ed.* **2016**, *55*, 1561–1564; *Angew. Chem.* **2016**, *128*, 1587–1590; e) D. P. August, G. S. Nichol, P. J. Lusby, *Angew. Chem. Int. Ed.* **2016**, *55*, 15022–15026; *Angew. Chem.* **2016**, *128*, 15246–15250; f) B. Roy, A. K. Ghosh, S. Srivastava, P. D'Solva, P. S. Mukherjee, *J. Am. Chem. Soc.* **2015**, *137*, 11916–11919; g) M. Yamashina, M. M. Sartin, Y. Sei, M. Akita, S. Takeuchi, T. Tahara, M. Yoshizawa, *J. Am. Chem. Soc.* **2015**, *137*, 9266–9269; h) S. Loffler, J. Lubben, L. Krause, D. Stalke, B. Dittrich, G. H. Clever, *J. Am. Chem. Soc.* **2015**, *137*, 1060–1063; i) J. E. M. Lewis, E. L. Gavey, S. A. Cameron, J. D. Crowley, *Chem. Sci.* **2012**, *3*, 778–784; j) N. Kishi, Z. Li, K. Yoza, M. Akita, M. Yoshizawa, *J. Am. Chem. Soc.* **2011**, *133*, 11438–11441; k) P. Liao, B. W. Langloss, A. M. Johnson, E. R. Knudsen, F. S. Tham, R. R. Julian, R. J. Hooley, *Chem. Commun.* **2010**, *46*, 4932–4934.
- [6] a) R.-J. Li, A. Marcus, F. Fadaei-Tirani, K. Severin, *Chem. Commun.* **2021**, *57*, 10023–10026; b) H. Takezawa, R. Tabuchi, H. Sunohara, M. Fujita, *J. Am. Chem. Soc.* **2020**, *142*, 17919–17922; c) G. H. Clever, W. Kawamura, S. Tashiro, M. Shiro, M. Shionoya, *Angew. Chem. Int. Ed.* **2012**, *51*, 2606–2609; *Angew. Chem.* **2012**, *124*, 2660–2663; d) J.-P. Bourgeois, M. Fujita, M. Kawano, S. Sakamoto, K. Yamaguchi, *J. Am. Chem. Soc.* **2003**, *125*, 9260–9261.
- [7] a) X. Tang, H. Jiang, Y. Si, N. Rampal, W. Gong, C. Cheng, X. Kang, D. Fairen-Jimenez, Y. Cui, Y. Liu, *Chem* **2021**, *7*, 2771–2786; b) C. J. Bruns, D. Fujita, M. Hoshino, S. Sato, J. F. Stoddart, M. Fujita, *J. Am. Chem. Soc.* **2014**, *136*, 12027–12034.
- [8] I. F. Mansoor, K. G. Dutton, D. A. Rothschild, R. C. Remsing, M. C. Lipke, *J. Am. Chem. Soc.* **2021**, *143*, 16993–17003.
- [9] a) S. M. Jansze, G. Cecot, M. D. Wise, K. O. Zhurov, T. K. Ronson, A. M. Castilla, A. Finelli, P. Pattison, E. Solari, R. Scopelliti, G. E. Zelinskii, A. V. Volgzhana, Y. Z. Voloshin, J. R. Nitschke, K. Severin, *J. Am. Chem. Soc.* **2016**, *138*, 2046–2054; b) D. K. Chand, K. Biradha, M. Kawano, S. Sakamoto, K. Yamaguchi, M. Fujita, *Chem. Asian J.* **2006**, *1*, 82–90.
- [10] The <sup>1</sup>H NMR data were fitted using the online tool provided on the following website: <http://supramolecular.org>. The 1:1 binding model represents a simplification, because the guest is [Li(BF<sub>4</sub>)<sub>4</sub>]<sup>3-</sup>, and not just Li<sup>+</sup>.
- [11] Deposition Numbers 2149704 (for [Pd<sub>4</sub>(L1)<sub>8</sub>LiBF<sub>4</sub>](BF<sub>4</sub>)<sub>8</sub>), 2157181 (for [Pd<sub>4</sub>(L1)<sub>8</sub>NaBF<sub>4</sub>](BF<sub>4</sub>)<sub>8</sub>), and 2130316 (for [Pd<sub>4</sub>(L2)<sub>8</sub>(LiBF<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](BF<sub>4</sub>)<sub>8</sub>) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.
- [12] W. M. Bloch, Y. Abe, J. J. Holstein, C. M. Wandtke, B. Dittrich, G. H. Clever, *J. Am. Chem. Soc.* **2016**, *138*, 13750–13755.
- [13] For a review about guest-induced transformations of coordination cages, see: E. G. Percastegui, *Eur. J. Inorg. Chem.* **2021**, 4425–4438.
- [14] For selected publications describing a guest-induced rearrangement of metal–ligand assemblies, see: a) T. K. Ronson, J. P. Carpenter, J. R. Nitschke, *Chem* **2022**, *8*, 557–568; b) D.-N. Yan, L.-X. Cai, P.-M. Cheng, S.-J. Hu, L.-P. Zhou, Q.-F. Sun, *J. Am. Chem. Soc.* **2021**, *143*, 16087–16094; c) L.-X. Cai, D.-N. Yan, P.-M. Cheng, J.-J. Xuan, S.-C. Li, L.-P. Zhou, C.-B. Tian, Q.-F. Sun, *J. Am. Chem. Soc.* **2021**, *143*, 2016–2024; d) K. Endo, H. Ube, M. Shionoya, *J. Am. Chem. Soc.* **2020**, *142*, 407–416; e) P.-M. Cheng, L.-X. Cai, S.-C. Li, S.-J. Hu, D.-N. Yan, L.-P. Zhou, Q.-F. Sun, *Angew. Chem. Int. Ed.* **2020**, *59*, 23569–23573; *Angew. Chem.* **2020**, *132*, 23775–23779; f) S. Wang, T. Sawada, K. Ohara, K. Yamaguchi, M. Fujita, *Angew. Chem. Int. Ed.* **2016**, *55*, 2063–2066; *Angew. Chem.* **2016**, *128*, 2103–2106; g) H. Lee, P. Elumalai, N. Singh, H. Kim, S. U. Lee, K.-W. Chi, *J. Am. Chem. Soc.* **2015**, *137*, 4674–4677; h) D. M. Wood, W. Meng, T. K. Ronson, A. R. Stefankiewicz, J. K. M. Sanders, J. R. Nitschke, *Angew. Chem. Int. Ed.* **2015**, *54*, 3988–3992; *Angew. Chem.* **2015**, *127*, 4060–4064; i) T. Sawada, H. Hisada, M. Fujita, *J. Am. Chem. Soc.* **2014**, *136*, 4449–4451; j) I. A. Riddell, M. M. J. Smulders, J. K. Clegg, Y. R. Hristova, B. Breiner, J. D. Thoburn, J. R. Nitschke, *Nat. Chem.* **2012**, *4*, 751–756; k) M. Scherer, D. L. Caulder, D. W. Johnson, K. N. Raymond, *Angew. Chem. Int. Ed.* **1999**, *38*, 1587–1592; *Angew. Chem.* **1999**, *111*, 1689–1694; l) S. Hiraoka, M. Fujita, *J. Am. Chem. Soc.* **1999**, *121*, 10239–10240.
- [15] a) S.-C. Li, T. Zhang, X.-P. Deng, X.-Q. Guo, L.-P. Zhou, F. Guo, Q.-F. Sun, *Inorg. Chem. Commun.* **2018**, *92*, 69–73; b) S. Kai, T. Tateishi, T. Kojima, S. Takahashi, S. Hiraoka, *Inorg. Chem.* **2018**, *57*, 13083–13086; c) K. Suzuki, M. Kawano, M. Fujita, *Angew. Chem. Int. Ed.* **2007**, *46*, 2819–2822; *Angew. Chem.* **2007**, *119*, 2877–2880.
- [16] C. Klein, C. Gutz, M. Bogner, F. Topic, K. Rissanen, A. Lutzen, *Angew. Chem. Int. Ed.* **2014**, *53*, 3739–3742; *Angew. Chem.* **2014**, *126*, 3814–3817.
- [17] a) Y.-H. Li, J.-J. Jiang, Y.-Z. Fan, Z.-W. Wei, C.-X. Chen, H.-J. Yu, S.-P. Zheng, D. Fenske, C.-Y. Su, M. Barboiu, *Chem.*

- Commun.* **2016**, *52*, 8745–8748; b) R. Zhu, J. Lübben, B. Dittrich, G. H. Clever, *Angew. Chem. Int. Ed.* **2015**, *54*, 2796–2800; *Angew. Chem.* **2015**, *127*, 2838–2842; c) M. Fukuda, R. Sekiya, R. Kuroda, *Angew. Chem. Int. Ed.* **2008**, *47*, 706–710; *Angew. Chem.* **2008**, *120*, 718–722.
- [18] The crystallographic analysis of  $[\text{Pd}_4(\text{L}2)_8]^{8+}$  reveals tight encapsulation of  $\text{LiBF}_4(\text{H}_2\text{O})$ . Therefore, in experiments with LiOTf, the guest is also expected to be  $\text{LiBF}_4(\text{H}_2\text{O})$ , with  $\text{BF}_4^-$  coming from the Pd salt.
- [19] For metal-based receptors with high selectivity for  $\text{Li}^+$  over  $\text{Na}^+$ , see: a) Z. Grote, M.-L. Lehaire, R. Scopelliti, K. Severin, *J. Am. Chem. Soc.* **2003**, *125*, 13638–13639; b) H. Piotrowski, K. Severin, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4997–5000; c) H. Piotrowski, G. Hilt, A. Schulz, P. Mayer, K. Polborn, K. Severin, *Chem. Eur. J.* **2001**, *7*, 3196–3208; d) H. Piotrowski, K. Polborn, G. Hilt, K. Severin, *J. Am. Chem. Soc.* **2001**, *123*, 2699–2700.
- [20] For a review about multicavity metallasupramolecular architectures, see: R. A. S. Vasdev, D. Preston, J. D. Crowley, *Chem. Asian J.* **2017**, *12*, 2513–2523.
- [21] T. Nakamura, H. Ube, M. Shionoya, *Chem. Lett.* **2013**, *42*, 328–334.
- [22] *Foldamers: Structure, Properties, and Applications* (Eds.: S. Hecht, I. Huc), Wiley-VCH, Weinheim, **2007**.
- [23] For a recent example of a  $\text{Pd}^{\text{II}}$ -based foldamer, see: D. Preston, *Angew. Chem. Int. Ed.* **2021**, *60*, 20027–20035; *Angew. Chem.* **2021**, *133*, 20180–20188.
- [24] Higher amounts of  $\text{D}_2\text{O}$  resulted in precipitation.
- [25] For homoleptic  $[\text{Pd}_n\text{L}_{2n}]^{2n+}$  assemblies with more than two chemical distinct ligands, see: a) M. Käseborn, J. J. Holstein, G. H. Clever, A. Lützen, *Angew. Chem. Int. Ed.* **2018**, *57*, 12171–12175; *Angew. Chem.* **2018**, *130*, 12349–12353; b) D. Fujita, Y. Ueda, S. Sato, N. Mizuno, T. Kumasaka, M. Fujita, *Nature* **2016**, *540*, 563–566.
- [26] For strategies to prepare low-symmetry metal–ligand assemblies, see: a) S. Pullen, J. Tessarolo, G. H. Clever, *Chem. Sci.* **2021**, *12*, 7269–7293; b) A. Goswami, S. Saha, P. K. Biswas, M. Schmittel, *Chem. Rev.* **2020**, *120*, 125–199; c) J. E. M. Lewis, J. D. Crowley, *ChemPlusChem* **2020**, *85*, 815–827; d) A. Ghosh, M. Schmittel, *Beilstein J. Org. Chem.* **2020**, *16*, 2831–2853; e) D. Bardhan, D. K. Chand, *Chem. Eur. J.* **2019**, *25*, 12241–12269; f) L. R. Holloway, P. M. Bogie, R. J. Hooley, *Dalton Trans.* **2017**, *46*, 14719–14723; g) W. M. Bloch, G. H. Clever, *Chem. Commun.* **2017**, *53*, 8506–8516; h) Z. He, W. Jiang, C. A. Schalley, *Chem. Soc. Rev.* **2015**, *44*, 779–789; i) M. Schmittel, *Chem. Commun.* **2015**, *51*, 14956–14968.
- [27] C. G. Pappas, P. K. Mandal, B. Liu, B. Kauffmann, X. Miao, D. Komáromy, W. Hoffmann, C. Manz, R. Chang, K. Liu, K. Pagel, I. Huc, S. Otto, *Nat. Chem.* **2020**, *12*, 1180–1186.

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