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Hierarchical Assembly of an Interlocked M_8L_{16} Container

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Abstract: *The self-assembly of eight Pd^{II} cations and sixteen phenanthrene-derived bridging ligands with 60° bite angles yielded a novel M_8L_{16} metallosupramolecular architecture composed of two interlocked D_{4h}-symmetric barrel-shaped containers. Mass spectrometry, NMR spectroscopy, and X-ray analysis revealed this self-assembled structure to be a very large "Hopf link" catenane featuring channel-like cavities, which are occupied by NO_3^- anions. The importance of the anions as catenation templates became imminent when we observed the nitrate-triggered structural rearrangement of a mixture of M_3L_6 and M_4L_8 assemblies formed in the presence of BF_4^- anions into the same interlocked molecule. Furthermore, the densely packed structure of the M_8L_{16} catenane was exploited in the preparation of a hexyloxy-functionalized analogue, which further self-assembled into vesicle-like aggregates in a reversible manner.*

Mechanically interlocked structures continue to spark scientific interest and curiosity owing to their aesthetic appeal and the dynamic properties that are introduced by the mechanical bond.[1] Although their preparation initially posed a synthetic challenge, the utilization of molecular templates[2] and the implementation of reversible covalent bonds[3] have resulted in high-yielding and facile syntheses. In this regard, the highly directional coordinative bond has been the basis of a variety of interpenetrated structures, such as catenanes,[4] rotaxanes,[5] knots,[6] Borromean rings,[7] and more.[8]

Among the plethora of possible metal and ligand combinations, Pd^{II} cations together with N-donor bridging ligands represent a robust and reliable combination widely utilized in the formation of hollow and interlocked metallosupramolecular structures.[8b,9] For assemblies obeying Pd_nL_{2n} stoichiometry ($n = 6, 12, 24, 30\ldots$), Fujita and co-workers have demonstrated the topological dependence of the structure of hollow polyhedra on obtuse ligand bite angles.[10] This work was recently expanded to the synthesis of a giant $Pd_{48}L_{96}$ Goldberg polyhedron.[10e] More acute ligand bite angles ($\geq 60°$) often yield Pd_3L_6 and Pd_4L_8 barrel-shaped containers or Pd_4L_8 doubly bridged tetrahedra (Figure 1),[11] whilst ligands with a parallel orientation of donors form lantern-shaped Pd_2L_4 coordination cages.[9] Catenation of the latter cages results in a larger family of Pd_4L_8 dimeric structures with a partitioned cavity capable of allosterically binding charged[12] and neutral[13] guest molecules. Under certain circumstances, these types of ligands also form a triply catenated link.[14] More recently, the close proximity of electron donor/acceptor moieties in mixed-ligand Pd_4L_8 interpenetrated cages has been exploited to study charge-transfer phenomena,[15] demonstrating that interlocked structures can also serve as platforms to examine interactions of densely packed functionalities.

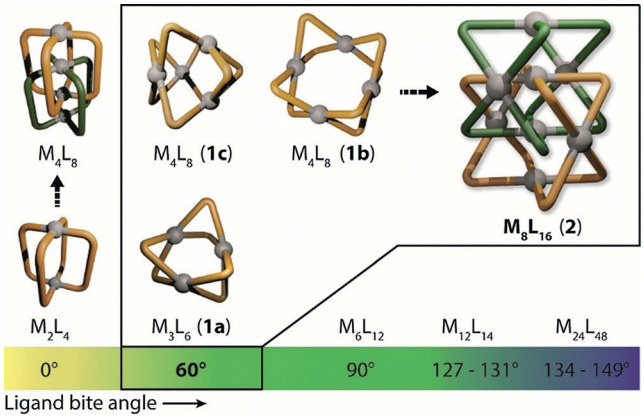

Figure 1. Comparison of the known M_nL_{2n} ($M = Pt^{II}$ or Pd^{II}) structures according to the bite angle of their constituent ligands with the catenated M_8L_{16} architecture **2**. Metal-mediated self-assembly of a ligand with a 60° bite angle can give rise to M_3L_6 (**1a**) or M_4L_8 structures (**1b** or **1c**). In previous studies, only M_2L_4 cage structures were shown to undergo catenation to give M_4L_8 interlocked dimers.

Despite the vast structural diversity of reported Pd_nL_{2n} polyhedral structures, interpenetrated assemblies larger than the Pd_4L_8 dimeric cages remained hitherto undiscovered. Herein, we report the assembly of an interlocked metallosupramolecule with the formula M_8L_{16} ($M = Pd^{II}$), which is the largest Pd_nL_{2n} catenane reported to date. Palladium-mediated self-assembly of the dimeric structure was achieved

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with $Pd(NO_3)_2$ and a rigid bis(monodentate) ligand L with a bite angle of 60°. The presence of NO_3^- anions is crucial for the formation of the large catenane, and can also trigger the structural rearrangement of a mixture of Pd_3L_6 and Pd_4L_8 assemblies formed in the presence of BF_4^- anions into the same interpenetrated structure. Through alkyl functionalization of the ligand backbone, an amphiphilic catenane was prepared that further self-assembled into vesicle-like aggregates, demonstrating that the densely packed nature of the Pd_8L_{16} architecture can be utilized as a platform for higher-order supramolecular aggregation.

Phenanthrene-based ligand L^1 (Figure 2) readily underwent self-assembly with $[Pd(CH_3CN)_4](BF_4)_2$ to form a D_{4h}-symmetric Pd_4L_8 (**1b**) container in DMSO as the only product.[11c] In CD_3CN, however, a 1:2:0.2 mixture of a D_{3h}-symmetric Pd_3L_6 (**1a**) container, **1b**, and a D_{2d}-symmetric

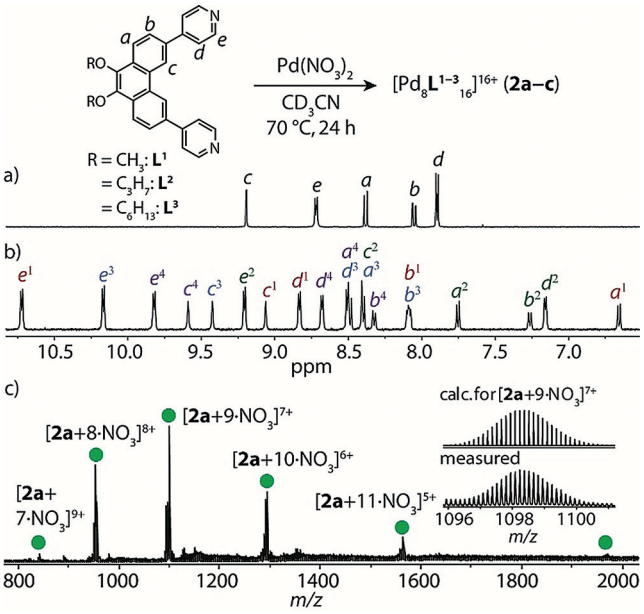

Figure 2. Top: Reaction equation representing the formation of Pd_8L_{16} (**2a–2c**). Bottom: ^1H NMR spectra (500 MHz, CD_3CN, 25 °C) of a) ligand L^1 and b) **2a**. c) ESI-MS spectrum of **2a** with the measured and calculated isotope patterns of $[2a + 9\,NO_3]^{7+}$ shown in the inset.

tetrahedron (**1c**) was obtained (Figure 1).[16] As both solvent and anion are known to dramatically affect the assembly of coordination cage structures,[9d,11] we carried out further investigations, including the reaction of L^1 with $Pd(NO_3)_2$. Self-assembly in the presence of nitrate anions again yielded **1b** as the major product in DMSO (Figure S10); however, in CD_3CN, we observed an entirely different outcome.

Heating a 2:1 mixture of L^1 and $Pd(NO_3)_2$ in CD_3CN at 70 °C for 24 h resulted in the quantitative formation of a new species (**2a**), as indicated by ^1H NMR spectroscopy and ESI mass spectrometry. In the ^1H NMR spectrum, a total of 20 aromatic signals were identified in the range of $\delta = 6.6$–10.7 ppm (compared with 5 aromatic signals for L^1), along with four signals in the region of the methoxy protons (Figures 2 and S11). ESI-MS analysis gave a spectrum with several prominent peaks consistent with the formula $[Pd_8L^1_{16} + n\,NO_3]^{(16-n)+}$ ($n = 7$–12; Figure 2c). By COSY NMR analysis, we identified four distinct sets of aromatic signals of equal ratios for L^1. Further analysis by ^1H-^1H NOESY revealed numerous cross-peaks (Figure S14), including notable through-space contacts between the H_c protons of sets 1/2 and 3/4. We therefore postulated that the fourfold splitting is due to L^1 being in two different chemical environments and losing its twofold symmetry in **2a**. The exclusive formation of **2a** was further confirmed by DOSY NMR analysis (Figure S16), which revealed that all of the assigned proton signals correspond to the same diffusion coefficient, with the derived hydrodynamic radius (1.24 nm) pointing towards a rather compact structure.

According to the empirical predictions for Pd_nL_{2n} assemblies,[10] a structure with a composition of Pd_8L_{16} is incompatible with a spherical, hollow topology, unless it is a transient intermediate towards larger $Pd_{12}L_{24}$ polyhedra.[10d] In light of the fourfold signal splitting observed in the ^1H NMR spectrum of **2a**, our $Pd_8L^1_{16}$ assembly is therefore likely to be composed of two interpenetrating $Pd_4L^1_8$ subunits. To gain insight into whether the possible monomeric Pd_4L_8 assemblies (**1b** or **1c**) are transient intermediates preceding **2a**, time-resolved ^1H NMR experiments were performed on a 2:1 mixture of L^1 and $Pd(NO_3)_2$ at 70 °C in MeCN (Figure S17). Only the proton resonances of **2a** evolved gradually over 20 h, and no other species were detected, suggesting that any intermediates involved in the self-assembly process are polymeric or short-lived in solution.

Owing to difficulties encountered with obtaining crystals of **2a** that are suitable for X-ray analysis, we focused on modifying the solubility of the catenane by utilizing a propoxy-functionalized ligand L^2. Under the same reaction conditions as for **2a**, the reaction of L^2 with $Pd(NO_3)_2$ gave an analogous Pd_8L_{16} interlocked structure (**2b**), as confirmed by ^1H NMR spectroscopy and ESI-MS analysis (Figures S18–S21). Single crystals (diffracting up to 1.28 Å with synchrotron radiation)[17] were grown by slow vapor diffusion of diisopropyl ether into a concentrated CD_3CN solution of **2b**, enabling unambiguous structure elucidation by X-ray crystallography. **2b** crystallized in the monoclinic space group $P2_1/n$, with one Pd_8L_{16} molecule in the asymmetric unit. The large interpenetrated structure, which is composed of two interlocked D_{4h}-symmetric containers,[18] can be described as a "Hopf link" (Figure 3) with D_{2d} symmetry.

In the structure of **2b**, the Pd_4L_8 monomers are geometrically related to one another by a 90° rotation along the major C_2 axis, creating an even partition of three channel-like cavities, each accommodating a NO_3^- counterion (Figure 3a). The central cavity is enclosed by phenanthrene moieties of L^2, which participate in offset π-stacking with an average separation of 3.7 Å. In contrast to the Pd_4L_8 interpenetrated cages,[8b] **2b** appears to be sterically restricted from mechanical movement owing to the respective tilt of the ligands between adjacent Pd_4L_8 units. In addition to the three NO_3^- anions found along the C_2 axis, four more (of a total of 13 located in the Fourier difference map) were found within the interpenetrated structure; however, not all of them occupied defined cavities. For example, **2b** contains four smaller cavities located perpendicular to the major C_2 axis along the

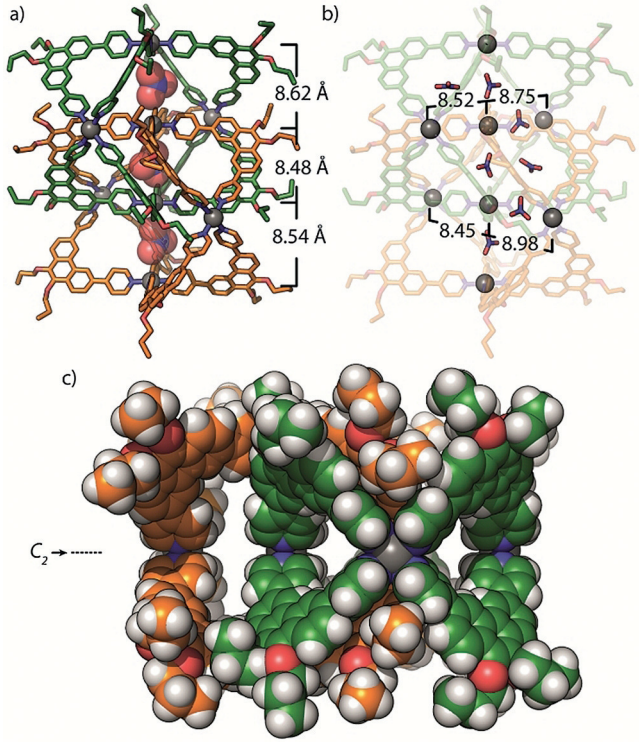

Figure 3. X-ray structure of **2b**:[24] a) Showing Pd···Pd distances and encapsulated NO_3^- anions along the major C_2 axis, b) highlighting the Pd···Pd distances of cations orthogonal to the major C_2 axis, c) a space-filling representation of the [2]catenane with NO_3^- anions removed for clarity.

Pd_3 planes (Figure 3b), with only two of the four cavities being occupied. Accordingly, the Pd···Pd separations for the empty cavities are 0.2–0.5 Å shorter than those of the filled cavities.[19]

Next, we examined whether NO_3^- anions trigger a transformative rearrangement of the mixture of **1a**, **1b**, and **1c** that is formed when L^1 is reacted with $[Pd(CH_3CN)_4](BF_4)_2$[16] in CD_3CN (during the course of our studies, a single crystal of **1c** was isolated and analyzed by X-ray crystallography, further supporting **1c** as one of the Pd-mediated assemblies of L^1; Figures 4b and S38–S40). The mixture of **1a**, **1b**, and **1c** was therefore heated at 70 °C for 24 h with 4, 8, and 12 equivalents of NO_3^-. In each case, ^{1}H NMR spectroscopy revealed that **2a** was formed exclusively (Figure 4); however, the reaction proceeded with the highest yield when 8 equivalents of NO_3^- were used (Figure S27). ESI-MS of this sample confirmed the structural conversion of **1a**–**1c** into **2a** as it revealed signals corresponding to $[Pd_8L^1_{16} + nX]^{(16-n)+}$ ($n = 8$–11, $X = Cl^-$, NO_3^-, and BF_4^-), with each signal distribution comprising a bias towards $X = 8\,NO_3^-$ and $(8-n)\,BF_4^-$ (Figure S28). To gain further insight into the role of the nitrate anions in the system, we performed the same transformation with a ^{15}N-labeled NO_3^- source. Inverse-gated ^{15}N NMR analysis revealed a single ^{15}N signal, which corresponds to the free $^{15}NO_3^-$ signal of the tetrabutylammonium salt used in the transformation (Figure S29). This indicates that the NO_3^- anions are not tightly bound and are free to exchange with free NO_3^- in the solvent, which is consistent with the channel-like cavities observed in the X-ray structure of **2b**. The reason for why catenation is observed only in the presence of NO_3^- anions could therefore be related to their optimal size as templates for this dimer.[12b,14,20] Indeed, **1a**–**1c** were not transformed into the catenated product upon extended heating (70 °C, 24 h) or in the presence of PF_6^- anions (Figures S9 and S31).

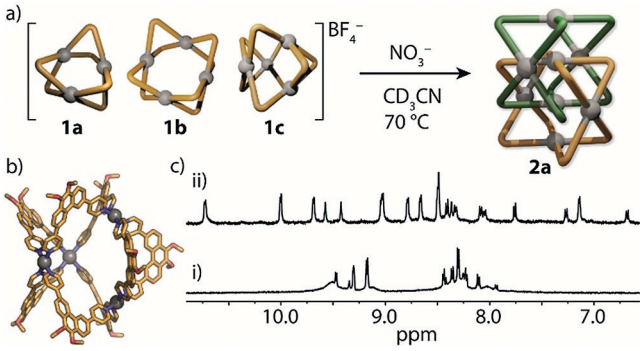

Figure 4. a) The NO_3^--mediated transformation of **1a**–**1c** into **2a**. b) X-ray structure of **1c**.[24] c) ^{1}H NMR spectra (500 MHz, CD_3CN) of i) **1a**–**1c** and ii) the same mixture after heating for 24 h in the presence of NO_3^- anions.

Finally, we examined whether the structurally dense nature of the Pd_8L_{16} [2]catenane can be utilized as a platform for further functionalization and supramolecular aggregation. It is worth noting that hierarchical aggregates of nanocages have scarcely been reported, and the underlying mechanisms of such systems primarily rely upon counterion-mediated interactions and π-stacking.[21] To promote a different aggregation pathway, we prepared a dihexyloxy-functionalized ligand (L^3) for the palladium-mediated self-assembly of amphiphilic catenane **2c** (Figures S22–S26). Remarkably, in MeCN, **2c** rapidly and spontaneously further self-assembled into a colloid of nanoscalar vesicular aggregates by virtue of the dense hydrophobic interactions between molecules of **2c** (Figure 5). This is in contrast to the behavior of **2a** and **2b**,

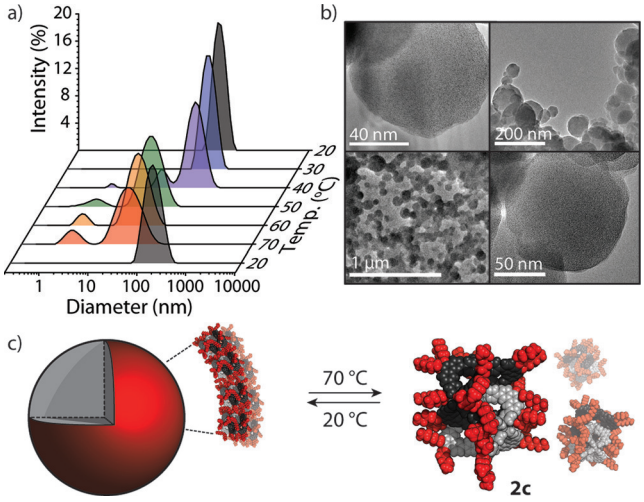

Figure 5. a) Variable-temperature DLS. b) TEM images of **2c**. c) Temperature-dependent aggregation of **2c** (plausible model based on the X-ray structure of **2b**).

which remain in solution owing to the shorter alkyl chains of their respective ligands. At 25 °C, a ^{1}H NMR spectrum of a cloudy solution of **2c** revealed the complete absence of proton resonances. At elevated temperatures (50–70 °C), however, the solution of **2c** became completely transparent, and the characteristic NMR spectroscopic signature of the interlocked molecule was observed (Figures S22 and S23). Dynamic light scattering (DLS) analysis of **2c** revealed particles with diameters of 150 ± 45 nm (PDI = 0.09) at 20 °C, which were observed to incrementally swell upon dilution (Figure S32), which is indicative of a vesicular-type assembly.[22] Variable temperature (VT) DLS revealed that this aggregate begins to disassemble between 40 and 50 °C, at which point a smaller aggregate (36.2 ± 20.4 nm) is formed along with particles measuring 2.3 ± 0.7 nm in diameter, the latter coinciding with the approximate dimensions of a single molecule of **2c**. Interestingly, cooling the sample back to 20 °C resulted in the recovery of the original, approximately 150 nm large aggregate (Figure 5a), with the MeCN solution becoming cloudy once again. The reversibility of the temperature-dependent supramolecular aggregation was demonstrated over three cycles by DLS with no detectable degradation (Figure S33). High-resolution TEM analysis of **2c** (Figures 5b and S34) confirmed the presence of spherical particles, albeit with a slightly broader distribution (80–200 nm).[23] This is in contrast to the TEM analysis of **2a**, which revealed small particles with diameters of approximately 3 nm, which correspond to non-aggregated molecules of **2a** (Figure S36). This observation further supports our hypothesis that the hydrophobic hexyloxy chains in **2c** promote hierarchical aggregation, which is facilitated by the structurally dense nature of this type of interlocked architecture.

In conclusion, we have reported the self-assembly of a 24-component Pd_8L_{16} [2]catenane composed of two interlocked D_{4h}-symmetric Pd_4L_8 barrel-shaped containers. The formation of the large catenane was shown to depend on the presence of NO_3^- counterions by NMR, ESI-MS, and crystallographic analysis. We also showed that NO_3^- anions can trigger the structural rearrangement of a mixture of Pd_3L_6 and Pd_4L_8 assemblies into the same interpenetrated product. Indeed, the X-ray crystal structure of **2b** revealed that the channel-like cavities are occupied by NO_3^- anions, which not only charge-balance the structure but also facilitate the interpenetration of the Pd_4L_8 barrel-shaped monomers. Exohedral functionalization of the structurally dense catenane with hexyloxy chains resulted in the hierarchical assembly of vesicle-like aggregates, which could be reversibly assembled and disassembled by a change in temperature. We are currently investigating the use of this aggregate as a molecular delivery and release vessel.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: catenanes · interlocked structures · self-assembly · structural transformations · supramolecular chemistry

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[1] a) J. F. Stoddart, *Chem. Soc. Rev.* **2009**, *38*, 1802–1820; b) M. S. Vickers, P. D. Beer, *Chem. Soc. Rev.* **2007**, *36*, 211–225; c) M. Janke, Y. Rudzevich, O. Molokanova, T. Metzroth, I. Mey, G. Diezemann, P. E. Marszalek, J. Gauss, V. Bohmer, A. Janshoff, *Nat. Nanotechnol.* **2009**, *4*, 225–229; d) J.-P. Collin, C. Dietrich-Buchecker, P. Gaviña, M. C. Jimenez-Molero, J.-P. Sauvage, *Acc. Chem. Res.* **2001**, *34*, 477–487; e) *Angew. Chem. Int. Ed.* **2016**, *55*, 13925; *Angew. Chem.* **2016**, *128*, 14129.

[2] a) C. D. Meyer, C. S. Joiner, J. F. Stoddart, *Chem. Soc. Rev.* **2007**, *36*, 1705–1723; b) K. M. Mullen, P. D. Beer, *Chem. Soc. Rev.* **2009**, *38*, 1701–1713; c) J.-F. Ayme, J. E. Beves, C. J. Campbell, D. A. Leigh, *Chem. Soc. Rev.* **2013**, *42*, 1700–1712; d) M. Denis, S. M. Goldup, *Nat. Rev. Chem.* **2017**, *1*, 61.

[3] a) G. Zhang, O. Presly, F. White, I. M. Oppel, M. Mastalerz, *Angew. Chem. Int. Ed.* **2014**, *53*, 5126–5130; *Angew. Chem.* **2014**, *126*, 5226–5230; b) T. Hasell, X. Wu, J. T. Jones, J. Bacsa, A. Steiner, T. Mitra, A. Trewin, D. J. Adams, A. I. Cooper, *Nat. Chem.* **2010**, *2*, 750–755.

[4] a) M. Fujita, *Acc. Chem. Res.* **1999**, *32*, 53–61; b) S. Prusty, S. Krishnaswamy, S. Bandi, B. Chandrika, J. Luo, J. S. McIndoe, G. S. Hanan, D. K. Chand, *Chem. Eur. J.* **2015**, *21*, 15174–15187; c) C. S. Wood, T. K. Ronson, A. M. Belenguer, J. J. Holstein, J. R. Nitschke, *Nat. Chem.* **2015**, *7*, 354–358.

[5] a) J.-P. Sauvage, *Acc. Chem. Res.* **1998**, *31*, 611–619; b) J. E. Beves, B. A. Blight, C. J. Campbell, D. A. Leigh, R. T. McBurney, *Angew. Chem. Int. Ed.* **2011**, *50*, 9260–9327; *Angew. Chem.* **2011**, *123*, 9428–9499.

[6] a) D. M. Engelhard, S. Freye, K. Grohe, M. John, G. H. Clever, *Angew. Chem. Int. Ed.* **2012**, *51*, 4747–4750; *Angew. Chem.* **2012**, *124*, 4828–4832; b) J. Guo, P. C. Mayers, G. A. Breault, C. A. Hunter, *Nat. Chem.* **2010**, *2*, 218–222; c) P. E. Barran, H. L. Cole, S. M. Goldup, D. A. Leigh, P. R. McGonigal, M. D. Symes, J. Wu, M. Zengerle, *Angew. Chem. Int. Ed.* **2011**, *50*, 12280–12284; *Angew. Chem.* **2011**, *123*, 12488–12492.

[7] a) S.-L. Huang, Y.-J. Lin, Z.-H. Li, G.-X. Jin, *Angew. Chem. Int. Ed.* **2014**, *53*, 11218–11222; *Angew. Chem.* **2014**, *126*, 11400–11404; b) K. S. Chichak, S. J. Cantrill, A. R. Pease, S.-H. Chiu,

G. W. V. Cave, J. L. Atwood, J. F. Stoddart, *Science* **2004**, *304*, 1308 – 1312.

[8] a) S. D. P. Fielden, D. A. Leigh, S. L. Woltering, *Angew. Chem. Int. Ed.* **2017**, *56*, 11166 – 11194; *Angew. Chem.* **2017**, *129*, 11318 – 11347; b) M. Frank, M. D. Johnstone, G. H. Clever, *Chem. Eur. J.* **2016**, *22*, 14104 – 14125; c) K. E. Horner, M. A. Miller, J. W. Steed, P. M. Sutcliffe, *Chem. Soc. Rev.* **2016**, *45*, 6432 – 6448; d) J. E. M. Lewis, P. D. Beer, S. J. Loeb, S. M. Goldup, *Chem. Soc. Rev.* **2017**, *46*, 2577 – 2591; e) R. S. Forgan, J.-P. Sauvage, J. F. Stoddart, *Chem. Rev.* **2011**, *111*, 5434 – 5464; f) S.-L. Huang, T. S. A. Hor, G.-X. Jin, *Coord. Chem. Rev.* **2017**, *333*, 1 – 26.

[9] a) G. H. Clever, P. Punt, *Acc. Chem. Res.* **2017**, *50*, 2233 – 2243; b) M. Han, D. M. Engelhard, G. H. Clever, *Chem. Soc. Rev.* **2014**, *43*, 1848 – 1860; c) W. M. Bloch, G. H. Clever, *Chem. Commun.* **2017**, *53*, 8506 – 8516; d) R. Chakrabarty, P. S. Mukherjee, P. J. Stang, *Chem. Rev.* **2011**, *111*, 6810 – 6918.

[10] a) Q.-F. Sun, J. Iwasa, D. Ogawa, Y. Ishido, S. Sato, T. Ozeki, Y. Sei, K. Yamaguchi, M. Fujita, *Science* **2010**, *328*, 1144 – 1147; b) J. Bunzen, J. Iwasa, P. Bonakdarzadeh, E. Numata, K. Rissanen, S. Sato, M. Fujita, *Angew. Chem. Int. Ed.* **2012**, *51*, 3161 – 3163; *Angew. Chem.* **2012**, *124*, 3215 – 3217; c) H. Yokoyama, Y. Ueda, D. Fujita, S. Sato, M. Fujita, *Chem. Asian J.* **2015**, *10*, 2292 – 2295; d) D. Fujita, H. Yokoyama, Y. Ueda, S. Sato, M. Fujita, *Angew. Chem. Int. Ed.* **2015**, *54*, 155 – 158; *Angew. Chem.* **2015**, *127*, 157 – 160; e) D. Fujita, Y. Ueda, S. Sato, N. Mizuno, T. Kumasaka, M. Fujita, *Nature* **2016**, *540*, 563 – 566.

[11] a) K. Suzuki, M. Kawano, M. Fujita, *Angew. Chem. Int. Ed.* **2007**, *46*, 2819 – 2822; *Angew. Chem.* **2007**, *119*, 2877 – 2880; b) S. Ganta, D. K. Chand, *Dalton Trans.* **2015**, *44*, 15181 – 15188; c) W. M. Bloch, Y. Abe, J. J. Holstein, C. M. Wandtke, B. Dittrich, G. H. Clever, *J. Am. Chem. Soc.* **2016**, *138*, 13750 – 13755; d) C. Klein, C. Gütz, M. Bogner, F. Topić, K. Rissanen, A. Lützen, *Angew. Chem. Int. Ed.* **2014**, *53*, 3739 – 3742; *Angew. Chem.* **2014**, *126*, 3814 – 3817; e) D. Samanta, A. Chowdhury, P. S. Mukherjee, *Inorg. Chem.* **2016**, *55*, 1562 – 1568; f) 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. Vologzhanina, Y. Z. Voloshin, J. R. Nitschke, K. Severin, *J. Am. Chem. Soc.* **2016**, *138*, 2046 – 2054; g) D. K. Chand, K. Biradha, M. Kawano, S. Sakamoto, K. Yamaguchi, M. Fujita, *Chem. Asian J.* **2006**, *1*, 82 – 90.

[12] a) S. Freye, J. Hey, A. Torras-Galán, D. Stalke, R. Herbst-Irmer, M. John, G. H. Clever, *Angew. Chem. Int. Ed.* **2012**, *51*, 2191 – 2194; *Angew. Chem.* **2012**, *124*, 2233 – 2237; b) S. Freye, R. Michel, D. Stalke, M. Pawliczek, H. Frauendorf, G. H. Clever, *J. Am. Chem. Soc.* **2013**, *135*, 8476 – 8479; c) R. Sekiya, M. Fukuda, R. Kuroda, *J. Am. Chem. Soc.* **2012**, *134*, 10987 – 10997; d) 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.

[13] S. Löffler, J. Lübben, L. Krause, D. Stalke, B. Dittrich, G. H. Clever, *J. Am. Chem. Soc.* **2015**, *137*, 1060 – 1063.

[14] R. Zhu, J. Lübben, B. Dittrich, G. H. Clever, *Angew. Chem. Int. Ed.* **2015**, *54*, 2796 – 2800; *Angew. Chem.* **2015**, *127*, 2838 – 2842.

[15] a) M. Frank, J. Ahrens, I. Bejenke, M. Krick, D. Schwarzer, G. H. Clever, *J. Am. Chem. Soc.* **2016**, *138*, 8279 – 8287; b) J. Ahrens, M. Frank, G. H. Clever, D. Schwarzer, *Phys. Chem. Chem. Phys.* **2017**, *19*, 13596 – 13603.

[16] W. M. Bloch, J. J. Holstein, W. Hiller, G. H. Clever, *Angew. Chem. Int. Ed.* **2017**, *56*, 8285 – 8289; *Angew. Chem.* **2017**, *129*, 8399 – 8404.

[17] A. Burkhardt, T. Pakendorf, B. Reime, J. Meyer, P. Fischer, N. Stübe, S. Panneerselvam, O. Lorbeer, K. Stachnik, M. Warmer, P. Rödig, D. Göries, A. Meents, *Eur. Phys. J. Plus* **2016**, *131*, 56.

[18] We use the term "container" to describe the general shape of the Pd_4L_8 D_{4h}-symmetric monomers.

[19] To obey the D_{2d} symmetry of the Pd_8L_{16} catenane, the NO_3^- anions are expected to rapidly exchange with free NO_3^- anions in solution.

[20] We note that catenation of this system is also dependent on CH_3CN as the solvent. The fact that catenation is not observed in DMSO may be due to DMSO solvent molecules stabilizing or packing more efficiently in the cavity of the D_{4h}-symmetric Pd_4L_8 momomer than CH_3CN; see Ref. [11a].

[21] a) D. Li, J. Zhang, K. Landskron, T. Liu, *J. Am. Chem. Soc.* **2008**, *130*, 4226 – 4227; b) D. Li, W. Zhou, K. Landskron, S. Sato, C. J. Kiely, M. Fujita, T. Liu, *Angew. Chem. Int. Ed.* **2011**, *50*, 5182 – 5187; *Angew. Chem.* **2011**, *123*, 5288 – 5293; c) H. Li, J. Luo, T. Liu, *Chem. Eur. J.* **2016**, *22*, 17949 – 17952; d) Y. Zhang, Q.-F. Zhou, G.-F. Huo, G.-Q. Yin, X.-L. Zhao, B. Jiang, H. Tan, X. Li, H.-B. Yang, *Inorg. Chem.* **2017**, https://doi.org/10.1021/acs.inorgchem.7b02777; e) J. K. Clegg et al., *Angew. Chem. Int. Ed.* **2010**, *49*, 1075 – 1078; *Angew. Chem.* **2010**, *122*, 1093 – 1096.

[22] a) D. E. Discher, A. Eisenberg, *Science* **2002**, *297*, 967 – 973; b) E. F. Marques, O. Regev, A. Khan, B. Lindman, *Adv. Colloid Interface Sci.* **2003**, *100 – 102*, 83 – 104; c) M. Sauer, W. Meier, *Chem. Commun.* **2001**, 55 – 56.

[23] The broader distribution may be due to partial desolvation and deformation of the vesicle-like aggregates because of solvent loss.

[24] CCDC 1811308 (**1c**) and 1811309 (**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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