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Self-Assembly

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A New Structural Motif for an Enantiomerically Pure Metallosupramolecular Pd_4L_8 Aggregate by Anion Templating**

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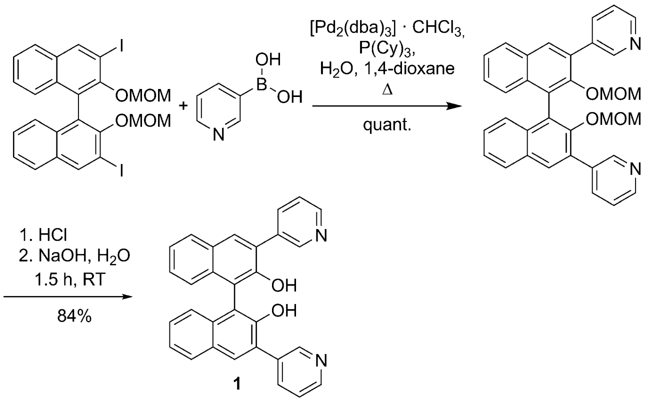
Dedicated to Professor Fritz Vögtle on the occasion of his 75th birthday

Abstract: *An enantiomerically pure BINOL-based bis(3-pyridyl) ligand **1** assembles into a homochiral* $[Pd_4(\mathbf{1})_8]$ *complex upon coordination to tetravalent* Pd^{II} *ions. The formation of this aggregate is templated by two tetrafluoroborate counterions that are encapsulated in two peripheral cavities. The resulting structure is a new structural motif for this kind of metallosupramolecular assemblies that arranges the palladium ions in a distorted tetrahedral fashion and forces ligand **1** to adopt two different conformations. Both phenomena are unique and cause an overall three-dimensional structure that has another confined, chiral, and hydrophilic central cavity.*

The use of tetravalent Pd^{II} and Pt^{II} ions and rigid bis(monodentate) bridging *N*-donor ligands has turned out to be one of the most successful approaches to access large three dimensional M_nL_{2n} metallosupramolecular aggregates by coordination-driven self-assembly.[1] In general, the outcome of such self-assembly processes can be predicted both in terms of composition and size of the closed 3D assemblies by assuming that the smallest assembly is formed according to the maximum occupancy rule that does not experience too much steric strain. Using a C-shaped bridging ligand structure with a proper bend angle and 3-pyridyl groups as metal binding motifs, therefore, usually gives rise to M_2L_4 aggregates.[2]

Recently, we were able to use this approach to demonstrate narcissistic self-sorting in the formation of homochiral Pd_2L_4 assemblies from bis(pyridine) ligands bearing chiral but rather flexible backbones based on 2,2′-dihydroxy-1,1′-binaphthyl (BINOL) cores.[3] Now, we have prepared another sterically rather congested ligand **1** of this type in racemic and enantiomerically pure form by Suzuki cross-coupling of 3,3′-diiodo-2,2′-dimethoxymethoxy-1,1′-binaphthyl with 3-pyridylboronic acid and subsequent deprotection of the hydroxy groups (Scheme 1).



Scheme 1. Synthesis of the axially chiral ligand **1**.

When we mixed 2 equivalents of enantiomerically pure **1** with one equivalent of $[Pd(CH_3CN)_4](BF_4)_2$ in acetonitrile and heated the solution to 70°C for 3 h we expected the straightforward formation of a homochiral complex $[Pd_2(\mathbf{1})_4](BF_4)_4$. Therefore, we were surprised to obtain an ESI mass spectrum that clearly revealed the formation of a $[Pd_4(\mathbf{1})_8]$ complex rather than the expected $[Pd_2(\mathbf{1})_4]$ aggregate (see the Supporting Information).

Among metallosupramolecular assemblies, this stoichiometry is rather rare and only three different kinds of structures for such aggregates have been reported. These are shown in Figure 1: The first is a crown-like metallamacrocycle in which two ligands bridge two metal centers.[4] This kind of structure has only been observed twice without any example

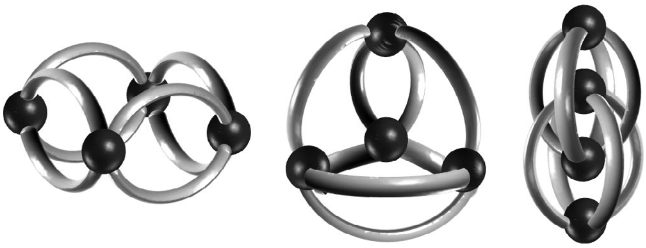


Figure 1. Representation of known M_4L_8 aggregates (dark gray spheres: palladium(II) ions; light gray arches: bridging ligands): crown-like metallamacrocyclic structure (left), tetrahedron-like aggregate (middle), and interlocked M_2L_4 cages (right).

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of 3-pyridyl groups yet described. The second has a tetrahedron-like arrangement of the metal ions in which two of the six edges of the tetrahedron are doubly bridged by two ligands, whereas the other four are only singly bridged by a single ligand.[5] This kind of assembly is even more rare, and in fact only a single ligand with a very rigid linear backbone and two 3-pyridyl units has been reported to form this type of structure upon coordination to tetravalent palladium(II) ions. Finally, a catenated structure has been reported in which two M_2L_4 cages are interlocked into each other.[6] This third variant has been observed in some cases and its formation is usually the result of anion template effects.

To gain an idea what the metallosupramolecular assembly looks like, we performed NMR experiments with optically pure **1**.[7] Again we obtained rather unexpected spectra. The ^{1}H NMR spectra, for example, shows a rather large but still well defined set of signals that contains four times as many signals as the ligand itself (Figure 2; Supporting Information).

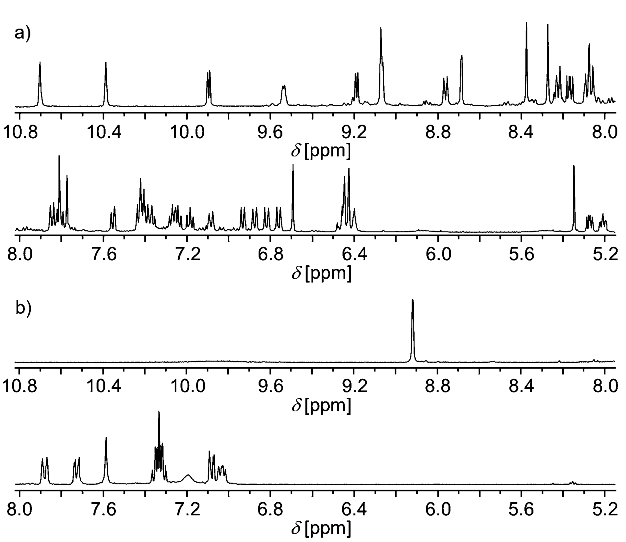

Figure 2. ^{1}H NMR spectra (500.1 MHz in [D$_3$]acetonitrile at 298 K) of a) the complex resulting from a 1:2 mixture of $[Pd(CH_3CN)_4](BF_4)_2$ and (*M*)-**1** and b) (*M*)-**1**.

2D H,H COSY, 2D ^{1}H,^{13}C HMQC, 2D ^{1}H NOESY, and 2D ^{1}H DOSY NMR experiments confirmed that all of these signals belong to a single species (with a larger size than ligand **1** alone or the initially expected $[Pd_2(\mathbf{1})_4]$ complex) rather than to a mixture of two or more different assemblies. None of the structures introduced above would give rise to such a spectrum because their ^{1}H NMR spectra would show sets of signals that would either have the same number of signals as the free ligand (crown-like macrocycle) or the doubled amount (tetrahedron-shaped and interlocked assemblies without encapsulated guests, with guest molecules in each of the three cavities, with one guest in the central cavity, or two guests in the two outer cavities). The four-fold amount, however, would only be possible with an interlocked assembly which would encapsulate two guest species in the central and one of the outer cavities or a guest in only one of the outer cavities.

Next we measured ^{19}F NMR spectra (Supporting Information). Interestingly, we found two different types of tetrafluoroborates present in solution in a relative ratio of 3:1. This indicates that our highly positively charged three-dimensional metallosupramolecular assembly interacts closely with two of the eight counterions most probably by encapsulation because we obtained two distinct signals rather than an averaged signal. Furthermore, we can conclude that these two anions should be encapsulated either in a single cavity or in two identical ones because we observe only a single signal for both. This, however, would rule out the formation of an interlocked structure in which only one of the outer cavities and the central cavity would each be filled by one anion, again indicating that our assembly must have a completely different structure.

Fortunately, we succeeded in growing crystals of our metallosupramolecular assembly by slow diffusion of diethyl ether into a solution of the complex in acetonitrile that could be analyzed by X-ray diffraction to finally solve the problem. As shown in Figure 3, our $[Pd_4(\mathbf{1})_8]$ assembly indeed has an unprecedented structural motif: it resembles a metallamacrocyclic structure in which two ligands bridge two metal centers like in the crown-like structure. However, the four palladium centers are not located at the corners of a square plane but rather at the vertices of a stretched tetrahedron with two short Pd–Pd distances of approximately 8.8 Å and four longer ones of about 14.0 Å.

This kind of arrangement makes it necessary that ligand **1** adopts two different conformations in the assembly, which is unique for these kinds of assemblies. The four ligands on the short edges adopt a slightly twisted C-shaped conformation in which the pyridine nitrogen atoms point more or less to the same side as the hydroxy groups of the BINOL core and the dihedral angle of the binaphthyl group is rather large ($\geq 90°$). The other four ligands, however, are found in a more extended twist-folded W-shaped conformation in which the nitrogen atoms of the pyridines point away from the hydroxy groups and the dihedral angle of the binaphthyl moiety is considerably smaller ($\leq 90°$). In total, this results in a three-dimensional structure that bears three cavities: two at the outer periphery that host two tetrafluoroborate anions, and another rather hydrophilic central cavity that hosts several acetonitrile molecules within the solid-state structure (Figure 3c). Thus, the structure can be divided into four independent subunits, each containing a palladium ion coordinated to four pyridine-substituted naphthyl moieties. This structure fits perfectly to all of our NMR spectroscopic observations, and we were able to assign all of the 40 different signals of the hydrogen atoms and the attached carbon atoms (see the Supporting Information).

It is important to note, however, that the use of tetrafluoroborate anions turned out to be crucial to obtain this structural motif, as nitrates for example did not even result in a defined assembly (see the Supporting Information). Thus, this is a rare example[6c,8] where the usually non-coordinating tetrafluoroborate ions act as efficient templates to ensure the selective formation of a metallosupramolecular aggregate. In fact, it takes only about 30 min at 70°C in

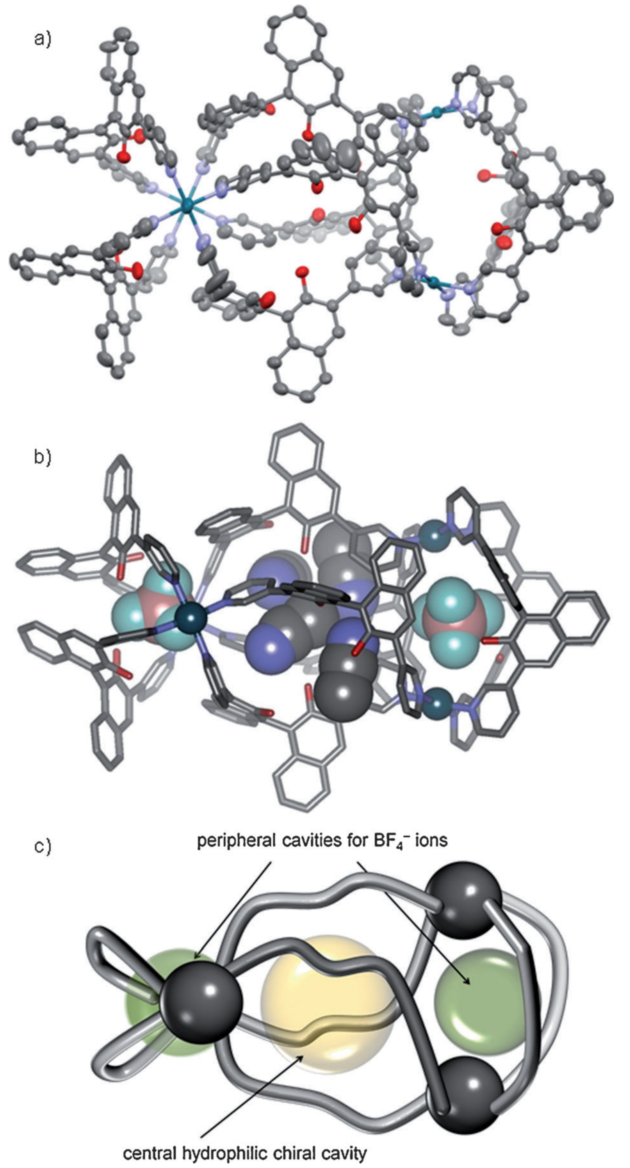

Figure 3. The structure of $[Pd_4\{(M)\text{-}\mathbf{1}\}_8](BF_4)_8$ as determined by X-ray diffraction analysis. C gray, N blue, O red, F green, B red-brown, Pd pale blue; H-atoms are omitted for clarity. a) Structure of the assembly without encapsulated solvent molecules and anions. b) Structure of the assembly including encapsulated CH_3CN molecules and BF_4^- ions (further non-encapsulated tetrafluoroborates and solvent molecules are omitted for clarity). c) Representation of the new structural motif (with truncated ligand structures).

acetonitrile to form this rather complicated structure (see the Supporting Information).

In summary, we were able to synthesize a dissymmetric bis(3-pyridyl) ligand **1** based on a BINOL scaffold. Upon coordination to tetravalent palladium(II) ions, enantiomerically pure **1** self-assembles into a metallosupramolecular $[Pd_4\{\mathbf{1}\}_8](BF_4)_8$ complex in acetonitrile. This unprecedented structural motif is obviously a result of an efficient template effect of two tetrafluoroborate counterions, which are encapsulated in the two peripheral cavities of the three-dimensional structure. Within this structure the four metal ions are arranged in a distorted tetrahedral fashion and four of the ligands adopt a C-shaped conformation whereas the other four adopt a twist-folded W-shaped arrangement. This leads to another central cavity which provides a confined, chiral, and hydrophilic environment.

Experimental Section

(*M*)-, (*P*), and (*rac*)–3,3′-Di(3-pyridyl)-2,2′-dihydroxy-1,1′-binaphthyl ({(*M*)-**1**}, {(*P*)-**1**}, and {(*rac*)-**1**}): 162 mg (0.31 mmol) of (*M*)-, (*P*)-, or (*rac*)-3,3′-di(3-pyridyl)-2,2′-di(methoxymethoxy)-1,1′-binaphthyl were dissolved in CH_2Cl_2 (10 mL). Conc. aq. HCl (6 mL) was then added dropwise. The resulting mixture was vigorously stirred at RT for 3 h. After that time, the mixture was neutralized with 6 M aq. NaOH. The aqueous phase was extracted three times with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$ and the solvent was removed under reduced pressure to give the product as an off-white solid. Yield 84 % (115 mg, 0.26 mmol). ^{1}H NMR (400.1 MHz, $CDCl_3$, 293 K) $\delta = 6.74$ (s, 2H, H-13), 6.78 (m, 2H, H-14), 7.21–7.31 (m, 8H, H-4, H-6, H-7, H-8), 7.58 (d, 2H, H-5, $^3J_{5,6} = 7.3$ Hz), 7.75 (d, 2H, H-15, $^3J_{14,15} = 7.5$ Hz), 9.15 (s, 2H, H-12), 11.10 ppm (br, 2H, H-9). ^{13}C NMR (100.6 MHz, $CDCl_3$, 293 K) $\delta = 115.7$ (C-1), 122.6 (C-14), 123.0 (C-6), 125.1 (C-8), 126.8 (C-7), 128.3 (C-5), 129.1 (C-3), 129.1 (C-8a), 130.0 (C-4), 134.1 (C-11), 135.2 (C-4a), 135.3 (C-15), 144.6 (C-13), 149.8 (C-12), 152.4 ppm (C-2). ESI MS (10 eV): $m/z =$ 441.2 ($[M+H]^+$), 463.2 ($[M+Na]^+$), 881.4 ($[2M+H]^+$), 903.4 ($[2M+Na]^+$). HR-MS (ESI): calcd. for $[C_{30}H_{20}O_2N_2+H]^+$ 441.1609, found 441,1603. Specific optical rotation: (*M*)-**1** $[\alpha]_D^{20} = -78\times10^{-1}\,cm^2g^{-1}$ ($c = 0.5$, CH_2Cl_2), (*P*)-(**1**) $[\alpha]_D^{20} = +80\times10^{-1}\,cm^2g^{-1}$ ($c = 0.5$, CH_2Cl_2). ECD {λ [nm] ($\Delta\varepsilon$ [$L\,mol^{-1}\,cm^{-1}$])}: (*M*)-**1**: 204 (51.6), 217 (−9.9), 237 (−21.7), 252 (20.8), 272 (−11.9), 291 (−2.8), 303 (–6.9), 329 (2.8), 350 (−1.6); (*P*)-**1**: 202 (–50.7), 216 (9.5), 237 (19,8), 250 (−19.1), 270 (13.5), 291 (3.3), 303 (6.5), 329 (2.0), 347 (2.9).

Preparation and characterization of the metal complexes: Ligand **1** (11.4 µmol, 5.0 mg) was dissolved in CD_3CN (0.4 mL). This solution was added to a solution of $[Pd(CH_3CN)_4](BF_4)_2$ (2.52 mg, 5.67 µmol) in CD_3CN (0.4 mL). The resulting solution was heated to 70 °C for 3 h and was then characterized by NMR spectroscopy. For ESI MS measurements, 60 µL of the NMR sample were attenuated with CH_3CN (930 µL). For the ECD spectroscopic measurements, 250 µL of the NMR solution were attenuated with CH_3CN (4.750 mL).

$[Pd_4\{(M)\text{-}1\}_8](BF_4)_8$ and $[Pd_4\{(P)\text{-}1\}_8](BF_4)_8$: ^{1}H NMR: (500.1 MHz, CD_3CN, 298 K) $\delta = 5.21$ (m, 4H, H-6D), 5.27 (dd, 4H, H-15C, $^3J_{15C,16C} = 5.7$ Hz, $^3J_{14C,15C} = 8.1$ Hz), 5.35 (s, 4H, H-9), 6.40 (m, 4H, H-7D), 6.42 (s, 4H, H-9), 6.44 (s, 4H, H-9), 6.45 (m, 4H, H-5D), 6.69 (s, 4H, H-9), 6.76 (d, 4H, H-8A, $^3J^7{}_{A,8A} = 8.5$ Hz), 6.82 (d, 4H, H-8C, $^3J_{7C,8C} = 8.6$ Hz), 6.87 (d, 4H, H-8D, $^3J_{7D,8D} = 8.1$ Hz), 6.93 (d, 4H, H-8B, $^3J_{7B,8B} = 8.3$ Hz), 7.08 (d, 4H, H-14C, $^3J_{14C,15C} = 8.1$ Hz), 7.19 (m, 4H, H-6A), 7.23–7.28 (m, 8H, H-6C, H-7A), 7.35–7.44 (m, 16H, H-6B, H-7B, H-7C, H-14D), 7.55 (d, 4H, H-5B, $^3J_{5B,6B} = 7.9$ Hz), 7.77 (s, 4H, H-4D), 7.81 (s, 4H, H-4B), 7.81 (dd, 4H, H-15B, $^3J_{15B,16B} = 5.7$ Hz, $^3J_{14B,15B} = 8.1$ Hz), 7.84 (d, 4H, H-5A, $^3J_{5A,6A} = 8.1$ Hz), 8.06–8.09 (m, 8H, H-15D, H-5C), 8.17 (dd, 4H, H-15A, $^3J_{14A,15A} = 8.2$ Hz, $^3J_{15A,16A} = 5.7$ Hz), 8.22 (d, 4H, H-14B, $^3J_{14B,15B} = 8.1$ Hz), 8.27 (s, 4H, H-4C), 8.37 (s, 4H, H-4A), 8.68 (s, 4H, H-12D), 8.76 (d, 4H, H-14A, $^3J_{14A,15A} = 8.2$ Hz), 9.07 (m, 8H, H-16B, H-12C), 9.19 (d, 4H, H-16D, $^3J_{15D,16D} = 4.9$ Hz), 9.54 (d, 4H, H-16C, $^3J_{15C,16C} = 5.7$ Hz), 9.89 (d, 4H, H-16A, $^3J_{15A,16A} = 5.7$ Hz), 10.39 (s, 4H, H-12B), 10.70 ppm (s, 4H, H-12A). ^{13}C NMR (100.6 MHz, CD_3CN, 293 K):$\delta = 112.9$ (C_q), 114.4 (C_q), 115.1 (C_q), 116.5 (C_q), 123.5 (C-6D), 124.2 (C-8C), 124.7 (C-15C), 124.9 (C-8A), 125.1 (C-8B), 125.6 (C-7A), 125.7 (C-7C), 125.9 (C-15D), 126.2 (C-7D), 126.4 (C-7B), 126.8 (C_q), 128.4 (C-5D), 128.9 (C-6C), 129.0 (C-6B), 129.1 (C-6A), 129.2 (C-15B), 129.3 (C-15A), 129.4 (C_q), 129.7 (C-5A), 129.8 (C-5C), 129.8 (C_q), 129.9 (C-5B), 130.0 (C-8D), 130.5 (C_q), 130.7 (C_q), 132.2 (C-4B), 132.3 (C-4C), 132.8 (C-4D), 133.3 (C-4A), 134.6 (C_q), 134.8 (C_q), 135.7 (C_q), 135.7 (C_q), 137.1 (C_q), 137.8 (C_q), 138.4 (C_q), 138.6 (C_q), 141.2 (C-14B), 141.2 (C-14A), 141.5 (C-14C), 142.9 (C_q), 143.5 (C-14D), 148.9 (C-16B), 149.4 (C_q), 149.8 (C-12C), 149.8 (C_q), 150.2 (C-16C), 150.3 (C_q), 150.8 (C_q), 150.9 (C-16A), 150.9 (C-16D), 151.5 (C_q), 151.5 (C-12D), 152.9 (C_q), 153.6 (C-12A), 154.5 ppm (C-12B). ^{19}F NMR (282.4 MHz, CD_3CN, 293 K): −150.2 (s, 6F, free BF_4^-), −146.2 (s, 2F, encapsulated BF_4^-). ^{1}H DOSY NMR (500.1 MHz, CD_3CN, 298 K): $D = 5.64 \times 10^{-10}\ m^2 s^{-1}$. MS: (ESI, 10 eV) $m/z = 1074.2$ ($\{[Pd_4(\mathbf{1})_8](BF_4)_4\}^{4+}$ and $\{[Pd_2(\mathbf{1})_4](BF_4)_2\}^{2+}$), 1461.3 (($\{[Pd_4(\mathbf{1})_8](BF_4)_5\}^{3+}$). ECD {$\lambda$ [nm] ($\Delta\varepsilon$ [$L\,mol^{-1}cm^{-1}$])}: $[Pd_4\{(M)\text{-}\mathbf{1}\}_8](BF_4)_8$: 207 (33.3), 233 (−18.0), 255 (17.9), 271 (−9.7), 305 (2.4), 324 (0.4), 345 (1.8).

For details of the X-ray crystallographic analysis of $[Pd_4\{(M)\text{-}\mathbf{1}\}_8](BF_4)_8$, see the Supporting Information. CCDC 982088 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] For some recent reviews, see: a) M. D. Ward, *Chem. Commun.* **2009**, 4487–4499; b) M. Yoshizawa, J. K. Klosterman, M. Fujita, *Angew. Chem.* **2009**, *121*, 3470–3490; *Angew. Chem. Int. Ed.* **2009**, *48*, 3418–3438; c) V. K. Jain, L. Jain, *Coord. Chem. Rev.* **2010**, *254*, 2848–2903; d) D. Yoshizawa, M. Fujita, *Bull. Chem. Soc. Jpn.* **2010**, *83*, 609–618; e) Y. Inokuma, M. Kawano, M. Fujita, *Nat. Chem.* **2011**, *3*, 349–358; f) R. Chakrabarty, P. S. Mukherjee, P. J. Stang, *Chem. Rev.* **2011**, *111*, 6810–6918; g) H. Amouri, C. Desmarets, J. Moussa, *Chem. Rev.* **2012**, *112*, 2015–2041; h) N. B. Debata, D. Tripathy, D. K. Chand, *Coord. Chem. Rev.* **2012**, *256*, 1831–1945.

[2] For some recent examples for the self-assembly of M_2L_4-cages using square-planar Pd^{II} metal centers, see: a) H. S. Sahoo, D. K. Chand, *Chem. Commun.* **2010**, *39*, 7223–7225; b) D. Tripathy, A. K. Pal, G. S. Hanan, D. K. Chand, *Dalton Trans.* **2012**, *41*, 11273–11275; c) 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; d) A. M. Johnson, R. J. Hooley, *Inorg. Chem.* **2011**, *50*, 4671–4673; e) N. Kishi, Z. Li, K. Yoza, M. Akita, M. Yoshizawa, *J. Am. Chem. Soc.* **2011**, *133*, 11438–11441; f) Z. Li, N. Kishi, K. Hasegawa, M. Akita, M. Yoshizawa, *Chem. Commun.* **2011**, *47*, 8605–8607; g) Z. Li, N. Kishi, K. Yoza, M. Akita, M. Yoshizawa, *Chem. Eur. J.* **2012**, *18*, 8358–8365; h) S. Ø. Scott, E. L. Gavey, S. J. Lind, K. C. Gordon, J. D. Crowley, *Dalton Trans.* **2011**, *40*, 12117–12124; i) G. H. Clever, W. Kawamura, M. Shionoya, *Inorg. Chem.* **2011**, *50*, 4689–4691; j) R. Sekiya, R. Kuroda, *Chem. Commun.* **2011**, *47*, 12346–12348; k) G. H. Clever, W. Kawamura, S. Tashirao, M. Shiro, M. Shionoya, *Angew. Chem.* **2012**, *124*, 2660–2663; *Angew. Chem. Int. Ed.* **2012**, *51*, 2606–2609; l) M. Han, R. Michel, B. He, Y.-S. Chen, D. Stalke, M. John, G. H. Clever, *Angew. Chem.* **2013**, *125*, 1358–1362; *Angew. Chem. Int. Ed.* **2013**, *52*, 1319–1323; m) C. Desmarets, T. Ducarre, M. N. Rager, G. Gontard, H. Amouri, *Materials* **2014**, *7*, 287–301.

[3] C. Gütz, R. Hovorka, G. Schnakenburg, A. Lützen, *Chem. Eur. J.* **2013**, *19*, 10890–10894.

[4] a) D. K. Chand, M. Fujita, K. Biradha, S. Sakamoto, K. Yamaguchi, *J. Chem. Soc. Dalton Trans.* **2003**, 2750–2756; b) K. Suzuki, M. Kawano, M. Fujita, *Angew. Chem.* **2007**, *119*, 2877–2880; *Angew. Chem. Int. Ed.* **2007**, *46*, 2819–2822.

[5] D. K. Chand, K. Biradha, M. Kawano, S. Sakamoto, K. Yamaguchi, M. Fujita, *Chem. Asian J.* **2006**, *1*, 82–90.

[6] a) M. Fukuda, R. Sekiya, R. Kuroda, *Angew. Chem.* **2008**, *120*, 718–722; *Angew. Chem. Int. Ed.* **2008**, *47*, 706–710; b) R. Sekiya, M. Fukuda, R. Kuroda, *J. Am. Chem. Soc.* **2012**, *134*, 10987–10997; c) S. Freye, J. Hey, A. Torras-Galán, D. Stalke, R. Herbst-Irmer, M. John, G. H. Clever, *Angew. Chem.* **2012**, *124*, 2233–2237; *Angew. Chem. Int. Ed.* **2012**, *51*, 2191–2194; d) J. Hey, I. Balcioglu, Y.-S. Chen, D. Stalke, T. Suenobu, S. Fukuzumi, H. Frauendorf, G. H. Clever, *Angew. Chem.* **2013**, *125*, 10288–10293; *Angew. Chem. Int. Ed.* **2013**, *52*, 10102–10106.

[7] Please note that we also performed experiments with (*rac*)-**1**. Although the Pd_4L_8 complex was again the major product, the self-assembly process was not completely selective in this case (see the Supporting Information). Therefore, narcissistic self-sorting is dominant but not exclusive.

[8] a) H. Amouri, L. Mimassi, M. N. Rager, B. E. Mann, C. Guyard-Duhayon, L. Raehm, *Angew. Chem.* **2005**, *117*, 4619–4622; *Angew. Chem. Int. Ed.* **2005**, *44*, 4543–4546; b) H. Amouri, C. Desmarets, A. Bettoschi, M. N. Rager, K. Boubekeur, P. Rabu, M. Drillon, *Chem. Eur. J.* **2007**, *13*, 5401–5407; c) C. Desmarets, C. Policar, L.-M. Chamoreau, H. Amouri, *Eur. J. Inorg. Chem.* **2009**, 4396–4400.