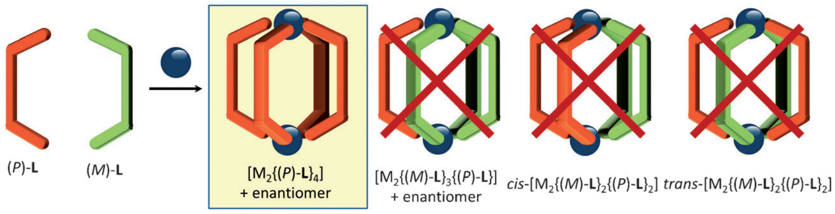

Sort yourself out! The self-assembly of a racemic dissymmetric bis(bipyridine) ligand based on a 1,1′-binaphthyl scaffold to a discrete, homochiral dinuclear metallosupramolecular [Pd_2L_4] cage upon coordination to palladium(II) ions proceeds through high-fidelity chiral self-sorting in a narcissistic, non-integrative, completive self-recognition manner (see scheme).

Supramolecular Chemistry

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Homochiral Supramolecular M_2L_4 Cages by High-Fidelity Self-Sorting of Chiral Ligands

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Homochiral Supramolecular M_2L_4 Cages by High-Fidelity Self-Sorting of Chiral Ligands

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Abstract: A 1,1′-binaphthyl-based bis(pyridine) ligand (**1**) was prepared in racemic and enantiomerically pure form to study the formation of $[Pd_2(\mathbf{1})_4]$ complexes upon coordination to palladium(II) ions with regard to the degree of chiral self-sorting. The self-assembly process proceeds in a highly selective narcissistic self-recognition manner to give only homochiral supramolecular M_2L_4 cages, which were characterized by ESI-MS, NMR, and electronic circular dichroism (ECD) spectroscopy, as well as by single-crystal XRD analysis.

Keywords: BINOL · palladium · self-assembly · self-sorting · supramolecular chemistry

Introduction

Self-sorting effects in the self-assembly of supramolecular aggregates from multicomponent mixtures have gained a lot of interest recently.[1] Successful approaches to high-fidelity self-sorting usually employ geometrical complementarity of size and shape to predetermine the outcome of the self-assembly process. In this sense, chiral self-sorting processes are a true challenge, because neither the size nor the shape varies, but only the relative spatial orientation. If there is any self-sorting at all, chiral recognition between enantiomers can, in principle, either lead to self-recognition or self-discrimination resulting in homo- or heterochiral assemblies, respectively, which Wu and Isaacs classified as narcissistic and social self-sorting processes.[2] However, both of these scenarios have been observed only in rather few cases in the formation of stereochemically defined metallosupramolecular aggregates from racemic ligands.[3,4]

Recently, we were able to show that racemic bis(nitrile) or bis(pyridine) ligands based on the chiral 2,8-difunctionalized Tröger's base scaffold undergo diastereoselective social self-sorting to heterochiral aggregates in a self-discriminating manner upon coordination to $[(dppp)Pd(OTf)_2]$ or $[(dppp)Pt(OTf)_2]$ (dppp = 1,3-bis(diphenylphosphino)propane).[5] In terms of the classifications of Schalley and coworkers[6] and Schmittel and Mahata,[7] this kind of self-sorting would also be integrative and 1^4-fold (3) completive,[8] because all the three different components of the mixture are part of the four particle assembly that is exclusively formed during the self-assembly process.

In contrast to this behavior, racemic bis(2,2′-bipyridine) and bis(pyridyl imine) ligands based on the Tröger's base scaffold with the same substitution pattern rather undergo narcissistic self-sorting in a nonintegrative but $2^{4,4}$-fold (3) completive[8] process resulting in the racemic mixture of the homochiral helicates.[3h,i,9] Interestingly, the same behavior was found in the self-assembly of dinuclear helicates from racemic bis(2,2′-bipyridine) ligands based on a 1,1′-binaphthyl core.[3e] Thus, we decided to study whether these also provide the necessary means to achieve a certain self-sorting behavior in the formation of metallosupramolecular aggregates that consist of more than four particles.

Because bis(pyridine) ligands are well established to form defined metallosupramolecular aggregates upon complexation with square-planar coordinated palladium(II) or platinum(II) ions, but also other ions,[10] we decided to prepare a 1,1′-binaphthyl derived bis(pyridine) ligand in racemic and enantiomerically pure form and study its self-assembly to metallosupramolecular M_2L_4 cages upon coordination to $[Pd(CH_3CN)_4](BF_4)_2$ with respect to the degree of chiral self-sorting.[11]

Results and Discussion

In an interesting manner, Johnson and Hooley could demonstrate that steric bulk can induce a considerable degree of self-sorting in the self-assembly of achiral M_2L_4 cages.[11l] Thus, ligand **1**, which has two 3-pyridyl groups linked by ethynyl bridges to the 1,1′-binaphthyl core in the 3- and 3′-positions was designed (Scheme 1). In addition, it contains methoxymethyl ether (MOM) groups in the 2- and 2′ positions, which should point inside the cavity of the metallosu-

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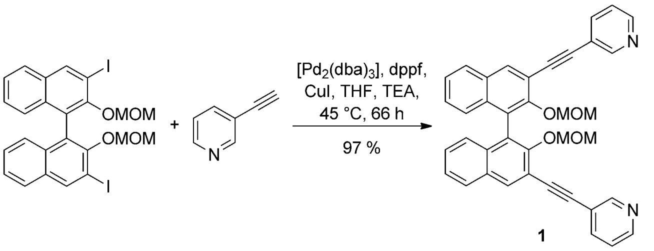


Scheme 1. Synthesis of ligand **1**.

pramolecular cage. Its synthesis could be achieved in excellent yield in a two-fold Sonogashira cross-coupling reaction of easily available 3,3′-diiodo-2,2′-bis(methoxymethyl)-1,1′-binaphthyl and commercially available 3-ethynylpyridine.

After synthesis of the ligand in enantiopure and racemic form, the next step was to investigate its coordination behavior towards Pd^{II} ions. Therefore, the 1,1′-bi-2-naphthol (BINOL) derivatives (*M*)-, (*P*)-, and (*rac*)-**1** were each dissolved in dichloromethane. Each solution was then mixed with a solution of $[Pd(CH_3CN)_4](BF_4)_2$ in acetonitrile in a stoichiometric ratio of 2:1. A series of mass and ^1H NMR spectra of these solutions recorded after keeping them at room temperature for different amounts of time revealed that the self-assembly process is rather slow (see the Supporting Information). Only after letting the mixture equilibrate for a total of one day at room temperature (or for 3 h at 55 °C) finally resulted in the formation of the desired coordination compounds, because the mass spectra (ESI) then showed that only [Pd$_2$**1**$_4$] species were present in the solutions (Figure 1).

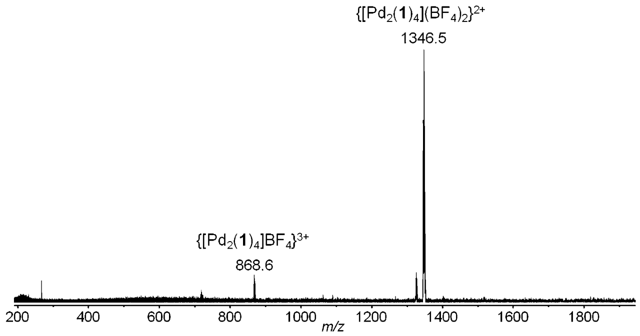
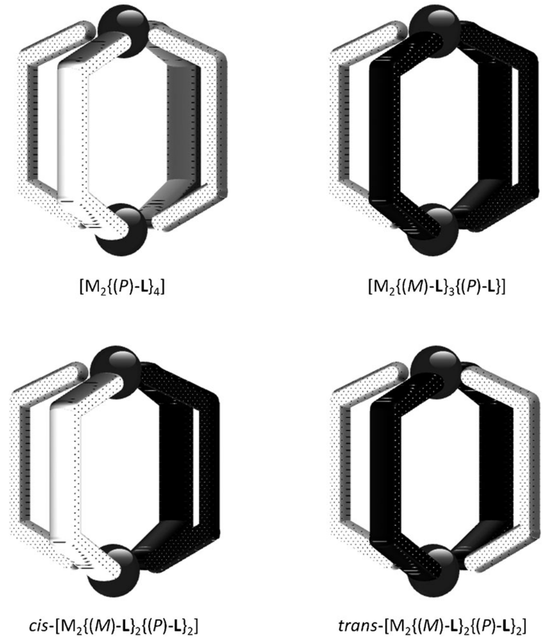


Figure 1. MS spectrum (ESI, positive mode) of a solution of $[Pd(CH_3CN)_4](BF_4)_2$ and ligand (*rac*)-**1** mixed in a 1:2 stoichiometry in acetonitrile/dichloromethane (1:1).



Scheme 2. Schematic representation of possible diastereoisomeric M^2**L**$_4$ complexes derived from racemic dissymmetric ligands (*M*)- and (*P*)-**L**.

Then ^1H NMR spectra were recorded to get information about the selectivity of the self-assembly process of the equilibrated mixture. Obviously, the enantiopure ligands can only form homochiral complexes and were only prepared for comparison. However, the situation is more complex in the case of the racemic ligand. In principle, six different assemblies can form herein (Scheme 2). These are the racemic pair of homochiral cages, the racemic pair of complexes containing three ligands of equal configuration and one of the other and two achiral but diasteromeric complexes that contain two ligands of equal configuration each that are either next to each other or opposite to each other in the 2:4 assembly.

From these the complexes with a 3:1 mixture of the stereoisomeric ligands do have the lowest symmetry and are expected to show the most complicated NMR spectra because the ligands are not all magnetically equivalent anymore and should therefore give rise to three sets of signals in a ratio of 1:2:1. However, in the other four assemblies, all the ligands would be magnetically equivalent, and hence, should give rise to a single set of signals of the same symmetry as the ligand itself. Because the two [Pd$_2${(*P*)-**1**}$_2${(*M*)-**1**}$_2$] complexes are diastereomers of the racemic pair of homochiral assemblies, however, they should differ considerably, and hence be distinguishable by comparison with the homochiral assemblies [Pd$_2${(*P*)-**1**}$_4$] and [Pd$_2${(*M*)-**1**}$_4$] obtained from optically pure (*P*)- or (*M*)-**1**, respectively.

The ^1H NMR spectra of the free ligand and the complexes of the enantiopure and the racemic ligands are shown in Figure 2. Analysis of these spectra allowed us to draw several conclusions: first of all, it clearly confirms the formation of discrete assemblies, because a set of sharp and considerably shifted signals for the complexes compared to that of the ligand was observed. But most importantly, the spectra of the complexes derived from the racemic ligands clearly revealed the highly selective formation of only a single diastereomer. Because the number of its resonances is equal to that of the ligand, we can rule out the formation of the racemic pair of [Pd$_2${(*P*)-**1**}$_3${(*M*)-**1**}] and [Pd$_2${(*M*)-**1**}$_3${(*P*)-**1**}$_1$] complexes. Further comparison with the homochiral complexes derived from the enantiomerically pure ligands allowed to identify the obtained complexes as the racemic

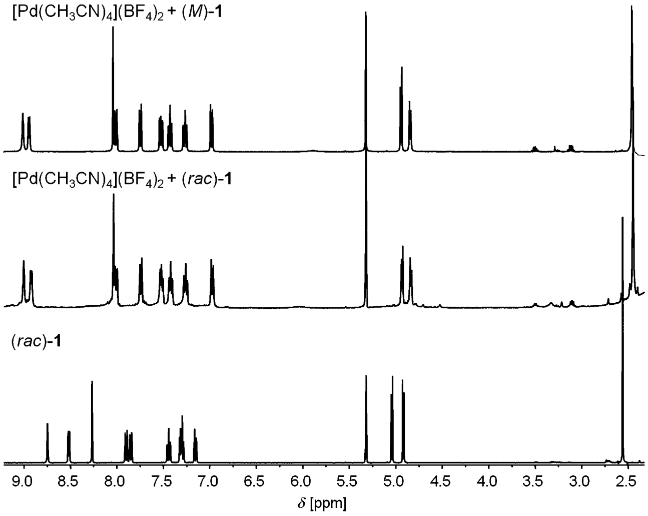


Figure 2. ^{1}H NMR spectra (400.1 MHz in CD_3CN/CD_2Cl_2 1:3, 293 K) of the free ligand (bottom) and of a solution of $[Pd(CH_3CN)_4](BF_4)_2$ and the (*rac*)-ligand (middle) or the (*M*)-enantiomer of the ligand (top) in a 1:2 stoichiometry ($c_0(\mathbf{1}) = 10.8\ \mathrm{mmol\,L^{-1}}$).

pair of homochiral assemblies, because it would be at least very unlikely that all of the proton signals of the diastereomeric $[Pd_2\{(M)\text{-}\mathbf{1}\}_2\{(P)\text{-}\mathbf{1}\}_2]$ complexes should be isochronic by coincidence. The same behavior was observed in pure acetonitrile or DMSO (see the Supporting Information). Thus, the self-assembly process proceeds with complete self-sorting in a narcissistic, non-integrative, $2^{6,6}$-fold (3) competitive self-recognition manner. Following the algorithm of Schmittel and Mahata,[7] the degree of self-sorting $M = P_0/P$, in which P_0 is the number of all possible aggregates (in our case six), and P is the number of all actually observed assemblies in the experiments (in our case two), can be calculated as $M = 3$.

To further ensure that the observed NMR signals really belong to the expected $Pd_2\mathbf{1}_4$ complexes, 2D-^{1}H-DOSY-NMR spectra were also recorded to obtain additional proof for the size of the aggregate and compare it to the calculated structure, and hence, its composition (Figure 3).

The measured diffusion coefficient of $D = 7.929\times 10^{-10}\ \mathrm{m^2 s^{-1}}$, which can be translated by the Stokes–Einstein equation and the correction for porous structures described by Macchioni and co-workers[12] to a hydrodynamic diameter of approximately 17.1 Å, which fits nicely to the calculated size between 17.2 and 23.3 Å.

Because we prepared the enantiomerically pure homochiral assemblies for comparison, we also decided to record their electronic circular dichroism (ECD) spectra to compare them with those of the enantiopure ligands (Figure 4). Interestingly, strong absorptions between $\lambda = 300$ and 360 nm were observed, which confirmed the formation of the enantiopure complexes.

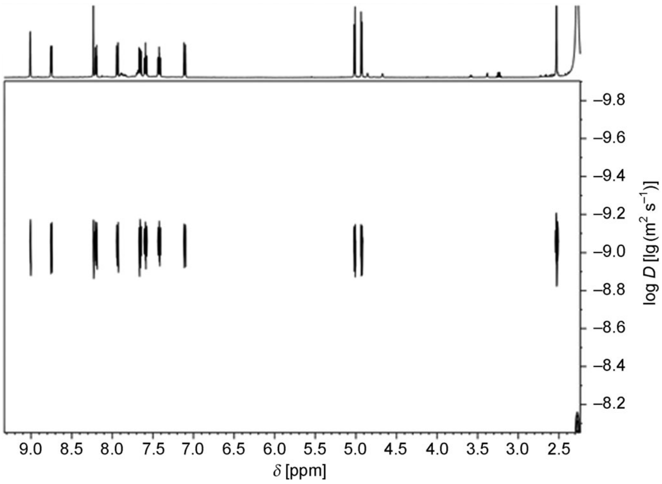


Figure 3. 2D ^{1}H-DOSY NMR spectrum (500.1 MHz in CD_3CN at 293 K) of $[Pd_2\{(P)\text{-}\mathbf{1}\}_4](BF_4)_4$ ($c = 2.7\ \mathrm{mmol\,L^{-1}}$).

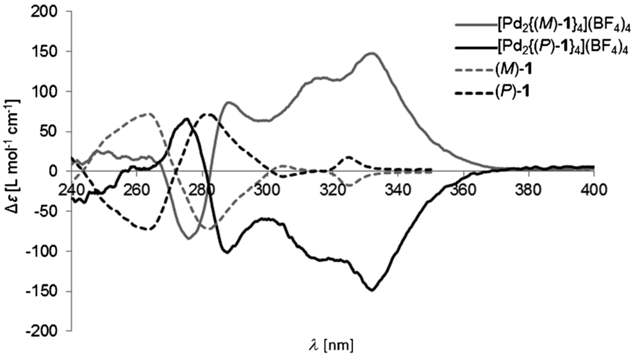


Figure 4. ECD spectra of the enantiomers of **1** and their corresponding dinuclear palladium complexes in acetonitrile (each $c = 67.7\ \mathrm{\mu mol\,L^{-1}}$).

Having characterized our assemblies in the gas phase and in solution, we also wanted to study their solid-phase structure. Single crystals suitable for XRD analysis were obtained by slow diffusion of diethyl ether into the solution of the $[Pd_2\{(P)\text{-}\mathbf{1}\}_4]$ complex in dichloromethane/acetonitrile (3:1). The crystal structure nicely confirmed our previous results obtained from MS and NMR data. The aggregate crystallized in the asymmetric triclinic space group $P\bar{1}$, and the structure of the metallosupramolecular cage is shown in Figure 5.

Conclusion

Dissymmetric bis(pyridine) ligand **1** was synthesized based on a 1,1′-binaphthyl scaffold in racemic, as well as enantiomerically pure, form. This ligand undergoes high-fidelity self-sorting upon coordination to $[Pd(CH_3CN)_4](BF_4)_2$ to form homochiral metallosupramolecular $Pd_2(\mathbf{1})_4$ cages in a narcissistic, non-integrative, $2^{6,6}$-fold (3) completive self-recognition manner. Following the algorithm of Schmittel and Mahata,[7] the degree of self-sorting $M = P_0/P$, could be calculated as $M = 3$. Thus, we were able to extent the concept of chiral self-sorting from dinuclear metallosupramolecular M_2L_2-rhombs to more complex dinuclear cage-like systems composed of six particles. This paves the avenue for further

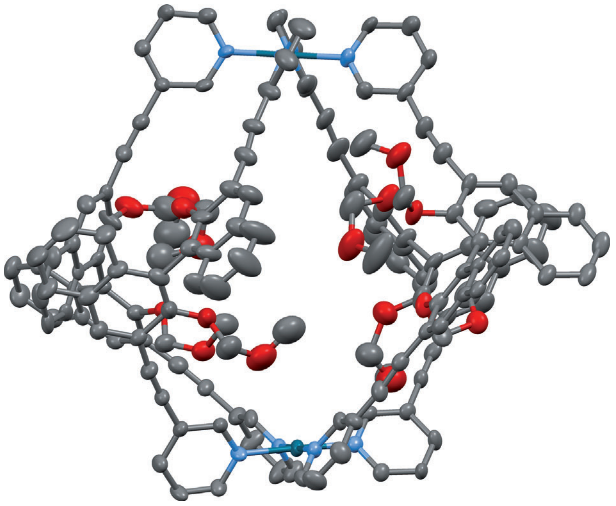


Figure 5. Supramolecular structures of $[Pd_2\{(P)\text{-}\mathbf{1}\}_4](BF_4)_4$ determined by XRD analysis (color code: grey carbon; blue nitrogen; red oxygen; and petrol palladium; solvent molecules, anions, and hydrogen atoms are omitted for clarity).

studies to explore the scope and limitations of chiral self-sorting in self-assembly processes to elucidate general principles that ensure narcissistic self-recognition or social self-discrimination.

Experimental Section

Reactions under inert gas atmosphere were performed under argon by using standard Schlenk techniques and oven-dried glassware. Thin layer chromatography was performed on aluminum TLC plates silica gel 60 F_{254} from Merck. Detection was carried out under UV light ($\lambda = 254$ and 366 nm). Products were purified by column chromatography on silica gel 60 (70–230 mesh) from Merck. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 500 spectrometer at 293 K, at 500.1 and 125.8 MHz, on a Bruker AM 400 at 293 K, at 400.1 MHz and 100.6 MHz, or a Bruker Avance 300 at 293 K at 300.1 MHz and 75.5 MHz, respectively. The ^{1}H NMR chemical shifts are reported in δ scale (ppm) relative to residual nondeuterated solvent as the internal standard. The ^{13}C NMR chemical shifts are reported in δ scale (ppm) relative to deuterated solvent as the internal standard. Signals were assigned on the basis of ^{1}H, ^{13}C, heteronuclear multiple-quantum correlation (HMQC), and heteronuclear multiple-bond correlation (HMBC) NMR experiments. Mass spectra were recorded at a microOTOF-Q or a Apex IV FTICR from Bruker. Elemental analyses were carried out with a HeraeusVario EL. However, CHN analyses could only be conducted with fluorine-free compounds. Most solvents were dried and distilled according to standard procedures, and were stored under argon. Enantiopure 2,2-dihydoxy-1,1′-binaphthyl and 3-ethynylpyridine were used as received (Alfa Aesar and Sigma–Aldrich). (*P*)-, (*M*)-, and (*rac*)-2,2-di(methoxymethoxy)-1,1′-binaphthyl were prepared by a literature procedure.[13,14]

Synthesis of (*P*)-, (*M*)-, and (*rac*)-3,3′-diiodo-2,2′-di(methoxymethoxy)-1,1′-binaphthyl:[14] To a solution of (*P*)-, (*M*)-, or (*rac*)-2,2′-di(methoxymethoxy)-1,1′-binaphthyl (2.12 g, 5.66 mmol) in dry THF (30 mL) at −78 °C, *sec*-butyllithium (16.58 mL, 23.21 mmol, 1.4 M in cyclohexane) was added, and the mixture was stirred for 1.5 h. After that time, iodine (8.62 g, 33.97 mmol) dissolved in dry THF (15 mL) was added, and the resulting solution was stirred at −78 °C for 15 h and for 3 h at RT. The reaction was quenched with methanol and saturated aqueous Na_2SO_3 solution. The solution was extracted three times with ethyl acetate, and the combined organic phases were dried over Na_2SO_4. Removing the solvent under reduced pressure led to the desired product in quantitative yield. The analytical data are in accordance with the published ones.[14]

Synthesis of (*P*)-, (*M*)-, and (*rac*)-2,2′-di(methoxymethoxy)-3,3′-bis(3-ethyndiyl-pyridyl)-1,1′-binapth® thyl (1): (*P*)-, (*M*)-, or (*rac*)-3,3′-diiodo-2,2′-di(methoxymethoxy)-1,1′-binaphthyl (150 mg, 0.24 mmol), 3-ethynylpyridine (71 mg, 0.5 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (11 mg, 9.6 µmol), 1,1′-bis(diphenylphosphino)ferrocene (dppf; 10.6 mg, 19.2 µmol), and CuI (8 mg, 38.3 µmol) were dissolved in dry triethyl amine (11 mL) and dry THF (4 mL) and stirred at 45 °C for 66 h. The reaction was quenched with saturated aqueous EDTA solution (30 mL). The resulting solution was extracted five times with dichloromethane, and the combined organic phases were dried over Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography on silica-gel with a mixture of cyclohexane/ethyl acetate/triethyl amine 4:3:1 as eluent ($R_f = 0.36$) to get the product as a yellow, pasty oil in 97 % yield. ^{1}H NMR (400.1 MHz, $CDCl_3$, 293 K): $\delta = 8.80$ (dd, $^4J_{H17,H14} = 2.1$, $^5J_{H17,H15} = 0.9$ Hz, 2H, H17), 8.55 (dd, $^3J_{H16,H15} = 4.9$ Hz, $^4J_{H16,H14} = 1.7$ Hz, 2H, H16), 8.26 (s, 2H, H-4), 7.87 (ddd, $^3J_{H5,H6} = 8.5$, $^4J_{H5,H7} = 1.2$, $^5J_{H5,H8} = 0.7$ Hz, 2H, H5), 7.83 (ddd, $^3J_{H14,H15} = 8.0$, $^4J_{H14,H17} = 2.1$, $^4J_{H14,H16} = 1.8$ Hz, 2H, H14), 7.45 (ddd, $^3J_{H7,H8} = 8.2$, $^3J_{H7,H6} = 6.9$, $^4J_{H7,H5} = 1.2$ Hz, 2H, H7), 7.32 (ddd, $^3J_{H6,H5} = 8.5$, $^3J_{H6,H7} = 6.9$, $^4J_{H6,H8} = 1.4$ Hz, 2H, H6), 7.29 (ddd, $^3J_{15,H14} = 8.0$, $^3J_{H15,H16} = 4.9$, $^5J_{H15,H17} = 0.9$ Hz, 2H, H15), 7.24 (ddd, $^3J_{H8,H7} = 8.2$, $^4J_{H8,H6} = 1.4$, $^5J_{H8,H5} = 0.7$ Hz, 2H, H8), 5.14 (d, $^2J_{H9,H9a} = -6.2$ Hz, 2H, H-9), 4.94 (d, $^2J_{H9a,H9} = -6.2$ Hz, 2H, H-9a), 2.54 ppm (s, 6H, H-10);^{13}C NMR (100.4 MHz, $CDCl_3$, 293 K): $\delta = 153.0$ (C2), 152.1 (C17), 148.7 (C16), 138.4 (C14), 134.6 (C4), 133.9 (C4a), 130.2 (C8a), 127.7 (C5), 127.6 (C-6); 126.5 (C8), 125.9 (C1), 125.7 (C7), 123.1 (C15), 120.4 (C13), 116.6 (C3), 99.0 (C9), 90.1 (C12), 89.7 (C11), 56.1 (C10); MS (ESI, 10 eV): *m*/*z* 599.2 $[M+Na]^+$, 577.2 $[M+H]^+$; HRMS (ESI): *m*/*z* calcd for $C_{38}H_{28}N_2O_4$ ($M_w = 576.64\ g\,mol^{-1}$) 577.2127 $[M+H]^+$; found: 577.2122.

Synthesis of $[Pd_2(1)_4](BF_4)_4$: To a solution of (*P*)- or (*M*)-, or (*rac*)-2,2′-di(methoxymethoxy)-3,3′-bis(3-ethyndiyl-pyridyl)-1,1′-binapththyl (5 mg, 8.67 µmol) in CD_2Cl_2 (0.6 mL) was added a solution of $[Pd(CH_3CN)_4](BF_4)_2$ (1.93 mg, 5.67 µmol) in CD_3CN (0.2 mL). The resulting mixture was stirred for one day at RT or for 3 h at 55 °C to get the desired complex in quantitative yield. ^{1}H NMR (400 MHz, CD_2Cl_2/CD_3CN 3:1, 293 K): $\delta = 9.01$ (s, 8H, H17), 8.94 (d, $^3J_{H16,H15} = 5.6$ Hz, 8H, H16), 8.04 (s, 8H, H4), 8.01 (ddd, $^3J_{H14,H15} = 8.0$, $^4J_{H14,H16} = 1.9$, $^4J_{H14,H17} = 1.2$ Hz, 8H, H14), 7.75 (d, $^3J_{H5,H6} = 8.2$ Hz, 8H, H5), 7.52 (dd, $^3J_{H15,H14} = 8.0$, $^3J_{H15,H16} = 5.6$ Hz, 8H, H15), 7.43 (ddd, $^3J_{H6,H5} = 8.1$, $^3J_{H6,H7} = 6.9$, $^4J_{H6,H8} = 1.1$ Hz, 8H, H7), 7.26 (ddd,$^3J_{H7,H8} = 8.6$, $^3J_{H6,H7} = 6.9$, $^4J_{H6,H8} = 1.0$ Hz, 8H, H6), 6.98 (d, $^3J_{H8,H7} = 8.6$ Hz, 8H, H8), 4.94 (d, $^2J_{H9a,H9b} = -5.9$ Hz, 8H, H9a), 4.84 (d, $^2J_{H9b,H9a} = -5.9$ Hz, 8H, H9b), 2.46 (s, 24H, H10); ^{1}H DOSY NMR (500.1 MHz, CD_3CN, 293 K): $\delta = 7.929 \times 10^{-10}\ m^2 s^{-1}$; MS (ESI, 10 eV): *m*/*z* 1346.5 $\{[Pd_2(\mathbf{1})_4](BF_4)_2\}^{2+}$, 868.6 $\{[Pd_2(\mathbf{1})_4](BF_4)\}^{3+}$.

Crystal-structure determination: *X-ray crystallographic analysis of $[Pd_2\{(P)\text{-}\mathbf{1}\}_4](BF_4)_4$*: Data were collected on a Bruker X8-Kappa-APEX II diffractometer equipped with a low-temperature device (Kryofelx I, Bruker AXS GmbH, Karlsruhe) by using graphite monochromatic $Mo_{K\alpha}$ radiation ($\lambda = 0.71071$ Å). The structure was solved by direct methods (SHELXL-97) and refined by full-matrix least squares on F^2 (SHELXL-97).[15] All nonhydrogen atoms were refined anisotropically. Hydrogen atoms at carbon atoms were placed in calculated positions and refined isotropically by using a riding model.

Crystal dimensions $0.12 \times 0.08 \times 0.05$ mm; colorless plates; $C_{152}H_{112}B_4F_{16}N_8O_{16}Pd_2$; $M_w = 2866.54\ g\,mol^{-1}$; triclinic; space group $P\bar{1}$; $a = 15.3148(5)$, $b = 16.5223(5)$, $c = 18.8622(5)$ Å; $\alpha = 69.520(2)$, $\beta = 67.529(2)$, $\gamma = 88.238(2)°$; $V = 4102.3(2)$ Å^3; $Z = 1$; $\rho = 1.160\ g\,cm^{-3}$; $\mu = 0.294\ mm^{-1}$; $F(000) = 1464$; 48156 reflections measured ($2\theta_{max} = 28.00°$; 33210 unique, $R_{int} = 0.0306$, completeness = 99.3 %); final R indices [$I > 2\sigma(I)$]; $R_1 = 0.0722$; $wR_2 = 0.1899$; R indices (all data): $R_1 = 0.1022$, $wR_2 = 0.2057$; GOF = 0.975 for 1791 parameters and 330 restraints; largest diff. peak and hole 1.710/−0.975 e Å^3, absolute stereochemical parameter $X = 0.00(2)$. CCDC-934122 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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