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Stereochemistry and chiroptical properties of bimetallic single helicates of hexapyrrole- α,ω -dicarbaldimines with high diastereoselectivity

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ABSTRACT: Bimetallic complexes of hexapyrrole- α,ω -dicarbaldimines consisting of a pair of four-coordinate metal sites adopt a helical closed C_2 -symmetric form or sigmoidal open forms depending on whether the 2,2'-bipyrrole subunit at the center of the hexapyrrole chain takes *cis*- or *trans*-conformation. X-ray crystallography of a bisNi complex having N-[(*R*)-1-cyclohexylethyl]carbaldimine units at both ends of the hexapyrrole chain revealed a non-symmetric heterohelical open form where the metal coordination sites of opposite helical sense sit on opposite sides of the central 2,2'-bipyrrole subunit. BisPd complexes preferred a closed C_2 form and a steric bulk at the 3,3'-position of the 2,2'-bipyrrole subunit improved the helical sense bias. A bisPd complex with N-[(*R*)-1-cyclohexylethyl]carbaldimine units adopts a helical closed C_2 form exclusively with full bias for a *P*-helical sense. These bimetallic single stranded helicates were reversibly oxidized to π -cation radicals at 0.1~0.3 V vs a ferrocene/ferrocenium couple and spectroelectrochemistry revealed remarkable absorption and CD spectral changes in the Vis-NIR region.

KEYWORDS: chiroptical molecular switch, helical structures, helicate, oligopyrrole, porphyrinoids, spectroelectrochemistry

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Dedicated to Emeritus Professor Hisanobu Ogoshi, Kyoto University, on the occasion of his 88th birthday

INTRODUCTION

Single stranded helicates

A number of helicates with high helical sense bias have been prepared by using oligomeric ligands (L) with a stereogenic center at both ends or in the linker [1-6]. A variety of stereochemically pure structures conveniently prepared by combination of metals and ligands have extensively been studied. For example, one-handed double and triple helicates (M_2L_2 and M_2L_3) are expected to find medicinal application based on their shape-selective affinity with biological helical materials [7-10]. Structures of single stranded helicates are flexible compared to double and triple stranded helicates. Their metal ions are externally accessible and able to act as an active center in various molecular functions such as asymmetric catalysis [11], in addition to the basic role of holding helical conformation. Long distance conformational control was demonstrated in the multimetallic single helicates (M_mL) of oligopyridines [11-19] and the related compounds [20-24] and of oligomeric ligands with multiple N_2O_2 square planar coordination sites [25-34]. However, multimetallic single helicates with a full bias of helical sense are limited to a few examples [11, 26].

Oligopyrrole helicates

Oligopyrroles composed of dipyrroin subunits are attractive ligands for helicates owing to their porphyrin-like nature. That is, anionic coordination to metal ions, intense absorption bands in the Vis-NIR region, and redox activity due to their π -conjugated system [35-41]. A number of open chain tetrapyrroles and related ligands (L) were used to generate single [35-46], double [47-58], triple [59-61], and cyclic helicates (M_mL_n) [62-65], and some enantiomerically pure monometallic single helicates (ML) were obtained by optical resolution [66-69]. Induction of helical chirality was demonstrated by introducing the point chirality or axial chirality to the tetrapyrrole ligands [70-76], and high helical sense bias (>90%) was achieved in some examples [72-76].

Although helicates of long chain oligopyrroles with more than five pyrrole units are interesting extension of this field [77-85], studies on their helical chirality are limited to a few examples of a M_2L -type because of their conformational diversity (Chart 1) [86-91]. Based on the successful control of helical chirality in the tetrapyrrolic bilinone Zn complexes [72-74], the bisZn complex (Zn_2L^1) of the dimeric bilinone ligand with (*R,R*)-point chirality in the linker was studied to show very high (>95%) diastereoselectivity in favor of the (*P,P*)-helical form [86,87]. We reported that bisNi benzenehexapyrrole- α,ω -dicarbaldimines (Ni_2L^2) and bisPd hexapyrrole- α,ω -dicarbaldimines (Pd_2L^3) where the (*R*)-point chirality at both ends (R^*) induces the (*P*)-helical chirality at each four-coordinate metal site with the (*P*)-axial chirality at the central π -conjugated subunit [90,91].

While stereocontrol of Ni_2L^2 (>96% diastereoselectivity) is better than that of Pd_2L^3 (85%), more effective π -conjugation is expected for Pd_2L^3 as inferred from its UV-vis absorption band at 699 nm that is at much longer wavelength than 566 nm of Ni_2L^2 . This electronic structure of Pd_2L^3 is attractive in developing functional materials utilizing redox chemistry and chiroptical properties in the Vis-NIR region. Here, we are extending our study on bimetallic single helicates of hexapyrrole- α,ω -dicarbaldimines (M_2L^3) based on our previous papers on Pd_2L^3 (**4aPd**) [91] and on bisPd and bisNi complexes of hexapyrrole- α,ω -dicarbaldehyde [83]. The effects of metals and the ligand substituents on the stereochemistry and redox-tunable chiroptical properties are discussed in detail in this paper.

RESULTS AND DISCUSSION

Conformation of bisnickel(II) hexapyrrole- α,ω -dicarbaldimines

In our preceding study on the bimetallic complexes of hexapyrrole- α,ω -dicarbaldehyde **1a** and **1b**, a pair of 3N + O metal coordination sites is helically shaped and the central bisdipyririn π -conjugated unit is twisted (Scheme 1, top) [83]. These three components of local helicity designated as *M* or *P* specify their stereochemistry. X-ray crystallography of **1aCu** revealed conformations of a helical closed form, (*P,P,P*) or (*M,M,M*), and a sigmoidal open form, (*P,P,P*) or (*M,M,M*) (Scheme 1, bottom) [83]. As the terminal aldehydes in a helical closed form are at the opposite sides of the 2,2'-bipyrrole subunit, they come close together through rotation of one metal coordination site around the central C(pyrrole- α)-C(pyrrole- α) bond of the 2,2'-bipyrrole subunit to lead to a homohelical open form. A metal coordination site in the open forms can change helicity through flipping of the terminal formylpyrrole moiety to cause interchange between a homohelical open form and a heterohelical (*M,-P*)-open form. The latter may be fluttering between (*M,P,P*)- and (*M,M,P*)-open conformations (Scheme 1, bottom). The 3,3'-position of the 2,2'-bipyrrole subunit comes very close to the terminal aldehyde oxygen atom halfway along the path of both rotation and flipping. Therefore, steric bulk both at the 3,3'-position of the 2,2'-bipyrrole subunit and at the terminal aldehyde position causes significant influence not only on the kinetic stability but also on the thermodynamic stability of each conformation. The terminal aldehyde of **1aCu** and **1aNi** is readily converted into the N-alkylcarbaldimine that exerts a profound effect on the helical handedness of the bimetallic complexes if it is derived from optically active amines. In fact, biscopper(II) hexapyrrole- α,ω -dicarbaldimines, **2aCu**, **3aCu**, and **4aCu**, were obtained in 93%, 56%, and 72% yield, respectively, when **1aCu** was reacted with benzylamine, (*S*)-(-)-1-phenylethylamine, and (*R*)-(-)-1-cyclohexylethylamine in THF at reflux for 6 h (Scheme 2).

We have already demonstrated that **1aNi** adopts an open form in solution [83]. When **1aNi** was reacted with benzylamine, (*S*)-(-)-1-phenylethylamine, and (*R*)-(-)-1-cyclohexylethylamine at high temperature in a polar solvent (reflux in toluene/ethanol = 3/1) for 24 h, bisnickel(II) hexapyrrole- α,ω -dicarbaldimines, **2aNi**, **3aNi**, and **4aNi**, were obtained in 95%, 83%, and 80% yield, respectively, in a single conformation of an open form (Scheme 2). The reaction conditions used for **1aCu** resulted in the formation of those bisNi complexes as a mixture of conformational isomers that was evidenced by their complicated ^1H NMR spectra (ESI S1). **2aNi** showed a two-fold symmetric signal pattern in the ^1H NMR spectrum (Fig. 1, bottom). Singlets at $\delta = 9.89$ ppm and 6.99 ppm are associated with the 3,3'-proton (H14) of the 2,2'-bipyrrole subunit and the formimidoyl proton (H1), respectively (ESI S2). The high frequency chemical shift of H14 is indicative of open forms because the 2,2'-bipyrrole subunit in a *trans* conformation puts the 3,3'-proton (H14) very close to the Ni ion, as seen in the solid state structure of **1aCu** [83]. Such agostic metal-H geometry in the square planar d^8 metal complexes is known to induce a remarkable high frequency NMR chemical shift [92-98].

A non-symmetric spectral pattern in the ^1H NMR spectrum of **3aNi** is indicative of a heterohelical pair of Ni coordination sites (Fig. 1, top). A NOESY experiment (ESI S3 and S4) of **3aNi** showed two sets of signals that are sequentially correlated as depicted in Fig. 2. An NOE correlation peak was observed between a doublet at $\delta = 1.18$ ppm due to the methyl proton (H54) at the stereogenic center and a singlet at $\delta = 7.39$ ppm due to the formimidoyl proton (H1), but an NOE correlation peak of another formimidoyl proton (H30) at $\delta = 6.26$ ppm was seen against the N-benzyl phenyl proton (H64; identical with H68 due to rapid rotation of the phenyl group) at $\delta = 6.48$ ppm instead of the methyl proton (H62) at $\delta = 1.41$ ppm. Accordingly, the methyl group (C54) of the N-[(*S*)-1-phenylethyl]carbaldimine part is *syn* to the formimidoyl proton (H1) and the N-benzyl phenyl group (C63~C68) is *syn* to another formimidoyl proton (H30), which means that the N-[(*S*)-1-phenylethyl]carbaldimine parts, (C53~C60) and (C61~C68), of **3aNi** belong to the Ni coordination site of *M*-helix and *P*-helix, respectively, as depicted in Fig. 2.† This discussion is based on the reasonable presumption that the sterically least demanding hydrogen (H53 and H61) at the stereogenic center should be directed to the 2,2'-bipyrrole subunit in solution as revealed in the X-ray structure of **4aNi** (Fig. 3). The significant difference in the chemical shifts ($\delta = 7.39$ and 6.26 ppm) between two formimidoyl protons (H1 and H30) of **3aNi** with respect to those ($\delta = 6.99$ and 6.79 ppm) of **4aNi**

is also rationalized by the ring current effect of the N-benzyl phenyl group in the *M*-helical and *P*-helical coordination site, respectively (Fig. 1 and ESI S1). High-frequency singlets of **3a**Ni ($\delta = 10.75$ and 8.76 ppm) and of **4a**Ni ($\delta = 10.80$ and 9.06 ppm) due to the 3,3'-protons (H14 and H17) of the 2,2'-bipyrrole subunit are characteristic of an open form.

X-ray crystallography (Fig. 3)§ of **4a**Ni showed an open form as well as **1a**Cu, but a pair of metal coordination sites of **4a**Ni is heterohelical in contrast to the homohelical **1a**Cu [83]. Therefore, a pair of the end groups are separated by the central 2,2'-bipyrrole subunit in **4a**Ni, while they lie on the same face of the 2,2'-bipyrrole subunit in **1a**Cu. The 2,2'-bipyrrole subunit of **4a**Ni is highly planar with its twist angle of 175.3° (Table 1 and ESI S11). The 3,3'-hydrogens (H14 and H17) of the *trans*-2,2'-bipyrrole subunit are very close to the Ni atoms with distances of $2.42 \text{ \AA}$ (H17–Ni1) and $2.60 \text{ \AA}$ (H14–Ni2).∞ This agostic geometry explains high-frequency chemical shifts of H14 and H17 in their ^1H NMR (ESI S1). All the methine hydrogens (H53, H55, H61, and H63) in the N-[(*R*)-1-cyclohexylethyl]carbaldimine parts of **4a**Ni are directed to the 2,2'-bipyrrole plane with short distances of H61 to C16 ($2.65 \text{ \AA}$), H63 to C15 ($2.52 \text{ \AA}$), H53 to C16 ($2.59 \text{ \AA}$), H53 to C15 ($2.63 \text{ \AA}$), and H55 to N4 ($2.66 \text{ \AA}$). In the *M*-helical coordination site of Ni2,† the hydrogen (H61) at the stereogenic center is away from the formimidoyl hydrogen (H30) and the sterically most demanding cyclohexyl group (C63~C68) lies close to the dipyrin unit (N3, C7~C15, N4) of the *P*-helical coordination site of Ni1. On the other hand, the methyl group (C54) at the stereogenic center of the *P*-helical coordination site of Ni1 is *syn* to the formimidoyl hydrogen (H1) and its cyclohexyl group (C55~C60) is away from the dipyrin unit (N5, C16~C24, N6) of the *M*-helical coordination site of Ni2.

3aNi and **4a**Ni showed a CD 1st Cotton effect at $\lambda = 709 \text{ nm}$ with a negative sign and at $\lambda = 712 \text{ nm}$ with a positive sign, respectively (Fig. 4 and ESI S19). These CD spectra showed greater intensities ($\Delta\epsilon$) than those of the bisCu complexes. Since electronic transition within the bisdipyrin π -conjugated unit should be responsible for the 1st Cotton effect, the observed CD signal of considerable strength seems inconsistent with a mostly centrosymmetric bisdipyrin unit with a very planar 2,2'-bipyrrole conformation in the solid state structure of **4a**Ni. Since CD spectra provide an excellent probe for stereochemistry of helically π -conjugated chromophores [99,100], the conformation of **4a**Ni in the solid state may be different from that in solution. Thus, some conformational models of **3a**Ni and **4a**Ni were theoretically generated based on the X-ray atom coordinates of the hexapyrrole core of **4a**Ni. Models for a heterohelical open form of **3a**Ni with an N-C(pyrrole- α)-C(pyrrole- α)-N torsion angle of -145° , 180° , and 145° in the 2,2'-bipyrrole subunit were taken as starting conformations in the structure optimization using DFT calculation on the $\omega\text{B97XD}/\{6\text{-}31\text{G(d)}, \text{LANL2DZ for Ni}\}$ level to result in (*M,M,P*)-, (*M,-,P*)-, and (*M,P,P*)-models of **3a**Ni with the 2,2'-bipyrrole torsion angle of -151.3° , 178.9° , and 134.8° , respectively (Fig. 5, ESI S13 and S15).

The ^1H NMR signals due to the N-benzyl phenyl group (C63~C68) at the *P*-helical coordination site of Ni2 in **3a**Ni appear at a significantly lower frequency region ($\delta = 6.48$ (H64), 6.87 (H65), and 7.06 (H66) ppm) compared with those of the phenyl group (C55~C60) at the *M*-helical coordination site of Ni1 ($\delta = 7.14$ (H56) and $7.33\sim 7.40$ (H57, H58) ppm) (Fig. 1, top). These low-frequency shifts support a (*M,M,P*)-model where the phenyl group (C63~C68) at the *P*-helical coordination site of Ni2 is positioned very close to the dipyrin π -plane (N3, C7~C15, N4) of the *M*-helical coordination site of Ni1 (Fig. 5, left). The phenyl group (C63~C68) in the (*M,-,P*)-, and (*M,P,P*)-model is too far from the dipyrin unit (N3, C7~C15, N4) to undergo the magnetic anisotropic effect (Fig. 5, right). The observed NOE correlation between a quartet ($\delta = 4.04$ ppm) due to the methine proton (H53) at the stereogenic center of a *M*-helical site and a singlet at $\delta = 8.76$ ppm due to the 2,2'-bipyrrole proton (H17) is in agreement with the (*M,M,P*)-model of **3a**Ni where the distance H53–H17 ($2.33 \text{ \AA}$) is short enough to give NOE (Fig. 5, ESI S4, top, and S13). The low frequency chemical shifts observed for the cyclohexyl protons at $\delta = 0.26$ and -0.37 ppm (ESI S1 and S4, bottom) of **4a**Ni are similarly explained in terms of the magnetic anisotropic effect of the dipyrin unit in a (*M,P,P*)-open form (ESI S14). The distances of H53–H17 ($2.53 \text{ \AA}$) and H52–H14 ($2.54 \text{ \AA}$) in this (*M,P,P*)-model of **4a**Ni are also consistent with the NOE correlations between the methine proton (H53) at

$\delta = 2.38$ ppm and the bipyrrrole proton (H17) at $\delta = 9.06$ ppm and between the bipyrrrole proton (H14) at $\delta = 10.80$ ppm and the methyl proton (H52) at $\delta = 1.89$ ppm of the *gem*-dimethylmethylene unit (ESI S4, bottom).

UV-vis and CD spectra were then simulated by TD-DFT calculation on the ω B97XD/{6-31G(d), LANL2DZ for Ni} level (ESI S22). A theoretically simulated CD spectrum for the (*M,M,P*)-open form of **3a**Ni showed the strong 1st Cotton effect in a negative sign that is in accordance with the observed CD spectrum in Fig. 4 (ESI S22, left). A theoretically simulated (*M,P,P*)-conformation of **3a**Ni was suggested to give a strong positive CD 1st Cotton effect and a (*M,-,P*)-conformation should give a very weak CD 1st Cotton effect. Therefore, the ^1H NMR and CD spectrum of **3a**Ni can be rationalized in terms of a (*M,M,P*)-open form. The observed CD 1st Cotton effect of **4a**Ni was also consistent with the TD-DFT simulation for a (*M,P,P*)-open form in its sign and intensity (ESI S22, right). It was reported that TD-DFT simulation for the CD profile is normally applicable to the bisdipyrin chromophore with the central 2,2'-bipyrrrole subunit [101]. This relationship between the sign of the 1st Cotton effect and the DFT-optimized conformation is also consistent with the exciton chirality method based on the stereochemical arrangement of a couple of dipyrin chromophores in the bisdipyrin subunit [102,103].

Conformation of bispalladium(II) hexapyrrole- α,ω -dicarbaldimines

1aPd was reacted with benzylamine, (*S*)-(-)-1-phenylethylamine, and (*R*)-(-)-1-cyclohexylethylamine to afford bispalladium(II) hexapyrrole- α,ω -dicarbaldimines, **2a**Pd, **3a**Pd, and **4a**Pd, in 85%, 59%, and 80% yield, respectively, as a mixture of conformational isomers after chromatographic purification (Scheme 3). The most abundant conformers of **2a**Pd and **4a**Pd crystallized out and their closed C_2 form structures were determined by X-ray crystallography (*vide infra*) [83]. Especially, **4a**Pd was found to take a (*P,P,P*)-closed C_2 form and underwent conformational change at room temperature in CDCl_3 solution in two days to an equilibrium mixture of three conformers with a molar ratio of 85:6:9 (Fig. 6). The reaction conditions in these conformational changes of bisPd complexes are much milder than bisNi complexes that require refluxing in a mixture of toluene and ethanol for a day. The major conformer of **4a**Pd showed ^1H NMR signals due to the methyl protons (H31 and H32) of the *gem*-dimethylmethylene bridge at $\delta = 1.63$ and 0.87 ppm (Fig. 6, top). This low-frequency chemical shift of H32 is characteristic of a closed C_2 -symmetric form because it reflects magnetic circumstance inside the crevice between two palladium coordination sites as shown in the case of **1a**Pd [83]. A minor pair of singlets at $\delta = 8.72$ and 8.32 ppm of equal intensity (Fig. 6, bottom) are most likely associated with the 3,3'-protons (H14 and H17) of the 2,2'-bipyrrrole subunit of a non-symmetric heterohelical (*M,-,P*)-open form because homohelical open C_2 forms should be less stable due to steric crowding of the two N-alkylcarbaldimine parts with one another. Since four multiplets due to the methine protons (H53 and H61) at the stereogenic center of the N-[(*R*)-1-cyclohexylethyl]carbaldimine part appeared at $\delta = 2.99, 2.66, 2.57,$ and 2.28 ppm, the third component of **4a**Pd should be a closed C_2 form of the opposite helical sense to the major component. **2a**Pd showed three sets of signals of a two-fold symmetric signal pattern with a ratio of 8:2:1 in the ^1H NMR spectrum (ESI S6, bottom). The major component in a closed C_2 form shows singlets due to the methyl protons (H31 and H32) of the *gem*-dimethylmethylene bridge at $\delta = 1.64$ and 0.85 ppm and singlets due to the formimidoyl proton (H1) and the 3,3'-proton (H14) of the 2,2'-bipyrrrole subunit at $\delta = 7.03$ and 6.58 ppm. On the other hand, the minor components exhibited high-frequency shifted singlets at $\delta = 8.78$ and 8.52 ppm in a 1:2 intensity ratio. They are characteristic of open forms and associated with the 3,3'-proton (H14) of the 2,2'-bipyrrrole subunit of a homohelical open C_2 -symmetric form and a heterohelical open C_2 -symmetric form (Scheme 1). Signals due to the methyl protons (H31 and H32) of the *gem*-dimethylmethylene bridge in these minor components appeared in the normal chemical shift region ($\delta = 1.85, 1.78,$ and 1.74 ppm)†.

The ^1H -NMR spectrum of **3aPd** showed several sets of signals due to conformational isomers. The major one showed a two-fold symmetric spectral pattern of chemical shifts similar to the major component of **2aPd** (ESI S6). The methyl protons (H31 and H32) of the *gem*-dimethylmethylene bridge at $\delta = 1.62$ and 0.86 ppm are characteristic of a closed C_2 -symmetric form (ESI S6, middle). The chemical shift ($\delta = 7.34$ ppm) of the formimidoyl proton (H1) of the major closed C_2 form of **3aPd** (Fig. 7) is very similar to that ($\delta = 7.39$ ppm) of the *M*-helical coordination site of **3aNi** but not to that ($\delta = 6.26$ ppm) of the *P*-helical coordination site. Three singlets with equal intensity at $\delta = 9.20$, 8.79 , and 8.68 ppm are associated with the 3,3'-protons (H14 and H17) of the 2,2'-bipyrrole subunit of open forms, specifically, a non-symmetric heterohelical (*M*, $-$,*P*)-open form and a homohelical (*P*,*P*,*P*)-open C_2 -symmetric form in a 2:1 molar ratio (Fig. 7). A (*M*,*M*,*M*)-open C_2 form is unlikely to exist because of severe steric crowding of the two N-alkylcarbaldimine parts with one another as depicted in Fig. 7. The formimidoyl protons (H30) of the *P*-helical coordination site of those two open forms are associated with two of the four singlets at $\delta = 6.74$, 6.70 , 6.60 , and 6.52 ppm with equal intensity (Fig. 7). The formimidoyl proton (H1) in the *M*-helical coordination site of a (*M*, $-$,*P*) open form should be in the region of $\delta = 7.2\sim 7.5$ ppm, but it is buried in the massive signals in this region. The other two of the above four singlets are associated with two protons (H17 and H30) due to a (*P*,*P*,*P*)-closed C_2 form. Presence of diastereomeric (*P*,*P*,*P*)- and (*M*,*M*,*M*)-closed C_2 forms is also supported by the low-frequency shifted singlets due to the methyl protons of the *gem*-dimethylmethylene bridge at $\delta = 0.93$ and 0.86 ppm (H52 and H32; ESI S6, middle) in an integral ratio of 1:4. Therefore, **3aPd** is considered to consist of four components, a (*M*,*M*,*M*)-closed C_2 form, a (*M*, $-$,*P*)-open form, a (*P*,*P*,*P*)-open C_2 form, and a (*P*,*P*,*P*)-closed C_2 form, with a molar ratio of 4:2:1:1. This is consistent with the presence of five quartets at $\delta = 4.54$, 4.32 , 4.02 , 3.95 , and 3.81 ppm due to the methine protons (H53 and H61) at the stereogenic center of the N-[(*S*)-1-phenylethyl]carbaldimine part with an intensity ratio of 1:1:4:1:1 (ESI S6, middle).

The reactions of **1bPd** with benzylamine, (*S*)-(-)-1-phenylethylamine, and (*R*)-(-)-1-cyclohexylethylamine gave bispalladium(II) hexapyrrole- α,ω -dicarbaldimines, **2bPd**, **3bPd**, and **4bPd**, in 76%, 78%, and 83% yield, respectively, as a mixture of conformational isomers (Scheme 3). **2bPd** showed two sets of signals of a two-fold symmetric pattern with a ratio of 92:8 in the ^1H NMR spectrum (Fig. 8, bottom). The major component shows the methyl protons (H31 and H32) of the *gem*-dimethylmethylene bridge at $\delta = 1.61$ and 0.93 ppm that are characteristic of a closed C_2 form. A singlet due to the methyl proton (H41) at the 3,3'-position of the 2,2'-bipyrrole subunit of the major component appeared in a normal chemical shift region ($\delta = 1.77$ ppm), but the corresponding singlet due to the minor component appeared at $\delta = 3.12$ ppm. This high-frequency chemical shift of H41 very similar to that ($\delta = 3.15$ ppm) [83] of **1bNi** is characteristic of an open form. Singlets due to the formimidoyl proton (H1) of the both components of **2bPd** appeared at $\delta = 6.87$ and 6.73 ppm. **3bPd** also showed two sets of signals of a two-fold symmetric spectral pattern with a ratio of 89:11 at 20°C in the ^1H NMR (Fig. 8, middle). The major component shows a pair of singlets due to the methyl protons (H51 and H52) of the *gem*-dimethylmethylene bridge at $\delta = 1.60$ and 1.02 ppm and the minor component shows the corresponding singlets (H31 and H32) at $\delta = 1.58$ and 0.92 ppm. Those low-frequency shifted chemical shifts of H52 and H32 are characteristic of a closed C_2 form. Singlets due to the 3,3'-dimethyl proton (H42 and H41) of the 2,2'-bipyrrole subunit of the both components appeared in a normal chemical shift region ($\delta = 1.75$ and 1.94 ppm). Therefore, **3bPd** exists as a mixture of closed C_2 forms of opposite helical sense. The chemical shift of the formimidoyl proton (H1) at $\delta = 7.30$ ppm of the minor closed C_2 form of **3bPd** is very similar to that ($\delta = 7.34$ ppm) of the major closed C_2 form of **3aPd**. The low-frequency chemical shift of the formimidoyl proton (H30) at $\delta = 6.48$ ppm due to the major closed C_2 form of **3bPd** is explained in terms of the ring current effect of the phenyl group of the N-[(*S*)-1-phenylethyl]carbaldimine part belonging to the *P*-helical coordination site, as

seen in the case of **3a**Ni in Fig. 2 (right). Consequently, it is considered that the major closed C_2 form of **3b**Pd adopts a *P*-helix while the minor closed C_2 form of **3b**Pd and the major closed C_2 form of **3a**Pd adopt a *M*-helix. After recrystallization, the major closed C_2 form of **3b**Pd was obtained in more than 99% diastereoselectivity as proven by the ^1H NMR and this *P*-helical closed C_2 form changed to an equilibrium mixture of diastereomers with a molar ratio of 72:28 at 50 °C in 2 h in CDCl_3 solution (ESI S7). It is noteworthy that the helicity change in the closed forms of **3b**Pd occurred with intermediate open forms unseen. The ^1H NMR spectrum of **4b**Pd showed a single set of a two-fold symmetric signal pattern characteristic of a closed C_2 form with at least 99% diastereoselectivity (Fig. 8, top). The chemical shifts of H1 ($\delta = 7.07$ ppm), H53 ($\delta = 2.69$ ppm), H31 ($\delta = 1.62$ ppm), H32 ($\delta = 0.94$ ppm), and H54 ($\delta = 0.52$ ppm) are very similar to those ($\delta = 7.09, 2.66, 1.63, 0.87, \text{ and } 0.69$ ppm, respectively) of the major component of **4a**Pd. Conformational change of **4b**Pd was not observed in the ^1H NMR spectrum at 50 °C for 5 h in CDCl_3 solution. Introduction of methyl groups at the 3,3'-position of the 2,2'-bipyrrole subunit not only caused higher preference for a closed C_2 form to open forms but also improved helical sense bias between a diastereomeric pair of closed C_2 forms in these bisPd complexes.

X-ray crystallography revealed the structures of **2a**Pd, **2b**Pd, and **4a**Pd in a closed form (Fig. 9)§. The methyl protons (H32 and H52) of the *gem*-dimethylmethylene bridge are directed to the formimidoylpyrrole rings of the opposite side with distances of 2.7~2.8 Å¶ (Fig. 9, bottom). This geometrical feature is consistent with the observed low-frequency shifts of H32 and H52 in the ^1H NMR spectra of their major components. **2a**Pd and **2b**Pd crystallized as a racemate and a *P*-helical enantiomer is displayed in their X-ray diagrams (Fig. 9, left and center). The *pro-S* hydrogens (H53 and H60) of the N-benzyl methylene protons of **2a**Pd of *P*-helix are very close to the 2,2'-bipyrrole subunit (Fig. 9, left)#. The N-benzyl phenyl ring (C54~C59) of **2a**Pd lies face-to-face with the pyrrole ring (N4, C12~C15) that belongs to the same coordination site of Pd1. The distances of 3.2~3.6 Å** between the phenyl ring atoms (C54, C55, C59) and the pyrrole ring atoms (N4, C15, C12), and also between the phenyl ring atoms (C61, C62) and the pyrrole ring atoms (N5, C16, C17) suggest π - π stacking of those aromatic rings. On the other hand, the X-ray diagram of **2b**Pd of *P*-helix revealed short distances between the *pro-R* hydrogens (H53' and H60') of the N-benzyl methylene protons and the 2,2'-bipyrrole subunit (Fig. 9, center)#. It is remarkable that the N-benzyl phenyl rings (C54~C59 and C61~C66) of **2b**Pd are away from the Pd coordination sites. As seen in the side views of **2a**Pd and **2b**Pd (Fig. 9, bottom), the twist angle (50.3°) of the *cis*-2,2'-bipyrrole subunit of **2b**Pd is much greater than that (22.6°) of **2a**Pd (Table 1). This large twist in **2b**Pd reduces the steric crowding of the 3,3'-dimethyl groups (C41 and C42) of the 2,2'-bipyrrole subunit, but it would bring the N-benzylcarbalimine parts (C53~C59 and C60~C66) very close to the 2,2'-bipyrrole subunit leading to serious steric hindrance unless the dipyrin units are curved. In fact, the plane-to-plane angles (18.4° and 22.2°) of the two pyrrole mean planes in the dipyrin units of **2b**Pd are twice as large as those (10.4° and 9.6°) of **2a**Pd (Table 1 and Fig. 9, bottom). Accordingly, the Pd-Pd distance (3.6293(8) Å) of **2b**Pd is only slightly longer than that (3.424(2) Å) of **2a**Pd in spite of their large difference in the twist angle of the *cis*-2,2'-bipyrrole subunit. Since the greater twist of the 2,2'-bipyrrole unit and the greater curving of the dipyrin units lead to the poorer π -conjugation of the bisdipyrin system, the major UV-vis absorption peaks of **2b**Pd, **3b**Pd and **4b**Pd (654, 651, and 648 nm) are at by ~50 nm shorter wavelength than those of **2a**Pd, **3a**Pd and **4a**Pd (701, 701, and 702 nm) (ESI S20).

3aPd is a mixture of four conformational isomers in the ratio of 4:2:1:1 based on the ^1H NMR analysis. A weak negative 1st Cotton effect observed at $\lambda = 689$ nm in the CD spectrum should reflect a spectral feature of the major closed C_2 form (Fig. 10 and ESI S20). It agrees with the theoretical CD spectrum simulated by TD-DFT calculation for the model of **3a**Pd in a closed C_2 form of *M*-helical sense (Scheme 4, left of top, and ESI S23). In contrast, **3b**Pd exhibited a strong positive 1st Cotton effect at $\lambda = 648$ nm (Fig. 10), while filtrate separated in the recrystallization of **3b**Pd exhibited a negative 1st Cotton effect at $\lambda = 643$ nm (ESI S21). The positive 1st Cotton effect observed for **3b**Pd as an equilibrium (92:8) mixture is

in accord with the CD spectrum simulated for a closed C_2 form of P -helical sense where the phenyl group of the N-[(S)-1-phenylethyl]carbaldimine part is *syn* to the formimidoyl hydrogen (Scheme 4, right of top, and ESI S16). Those CD spectral features of **3aPd** and **3bPd** are consistent with the stereochemistry inferred from the ^1H NMR analysis.

X-ray crystallography unambiguously revealed the conformation of a P -helical closed form of **4aPd** where the methine hydrogens (H53 and H61) at the stereogenic center of the N-alkylcarbaldimine part are very close to the 2,2'-bipyrrole subunit (Fig. 9, right)#. The observed strong CD 1st Cotton effects of **4aPd** and **4bPd** in a positive sign at $\lambda = 699$ and 646 nm, respectively (Fig. 10), are in agreement with the theoretical CD spectrum simulation by TD-DFT for a P -helical conformation (ESI S23). BisPd helicates **4a***Pd and **4b***Pd derived from the reaction of **1aPd** and **1bPd** with (S)-(+)-1-cyclohexylethylamine showed their mirror image CD spectra with a negative sign of the 1st Cotton effect (Fig. 10). X-ray structure of **4aPd** (Fig. 9, right) and the theoretically optimized P -helical conformation models of **4aPd** and **4bPd** (ESI S17 and S18) indicate that the 2,2'-bipyrrole subunit is twisted so as to circumvent steric crowding of its substituents (R^1 and R^2) with the cyclohexyl group of the N-[(R)-1-cyclohexylethyl]carbaldimine part (Scheme 4, left of bottom). On the other hand, the cyclohexyl group in the M -helical conformation models (ESI S17) would suffer from steric hindrance with the 2,2'-bipyrrole subunit due to its mismatching twist (Scheme 4, right of bottom). This stereochemical feature explains why both **4aPd** and **4bPd** prefer a P -helix and a larger twist in the 2,2'-bipyrrole subunit of **4bPd** improved diastereoselectivity. It is worthy of note that the methine hydrogens (H55 and H63) of the cyclohexyl group take an *anti* relationship with respect to the neighboring methine hydrogens (H53 and H61) at the stereogenic centers in the X-ray crystallography of **4aPd** (Fig. 9, bottom of right). This stereochemistry minimizes steric constraint within the N-alkylcarbaldimine parts, but it forces the cyclohexyl group of **4aPd** and **4bPd** to come closer to the 2,2'-bipyrrole subunit especially in a M -helical conformation (ESI S17). However, the phenyl group of the N-[(S)-1-phenylethyl]carbaldimine part in the case of **3aPd** and **3bPd** would not come close to the 2,2'-bipyrrole subunit even in a mismatching P -helical conformation because of the sp^2 hybridized C55 and C63 atoms (Scheme 4, right of top, and ESI S16). The observed moderate preference for a M -helix in **3aPd** and a P -helix in **3bPd** is explained in terms of the positional preference of the N-benzyl phenyl group of the N-[(S)-1-phenylethyl]carbaldimine part as is illustrated in the X-ray structures of **2aPd** and **2bPd**. Although the π - π stacking interaction between the phenyl group and the 2,2'-bipyrrole subunit of **3aPd** would contribute to favor a M -helix, the phenyl group of **3bPd** in a M -helix would be difficult to take a face-to-face orientation with the 2,2'-bipyrrole subunit because of the highly curved dipyrroin unit.

Since steric constraint between two metal coordination sites would be greater in a closed form than in a heterohelical open form, the bisdipyrroin system of a closed form takes greater twist leading to less effective π -conjugation. Therefore, a heterohelical open form was favored exclusively in the case of bisNi complexes. This steric constraint would be relieved in the bisPd complexes because of the longer Pd–N bonds by ca. 0.10 Å than the Ni–N bonds (Table 1), which may also be responsible for the lower barriers for conformational changes in the bisPd complexes than in the bisNi complexes. In addition, we pointed out in our previous paper that a weak Pd–Pd bonding contributes to stabilize a closed form of **1aPd** [83].

Redox-tunable chiroptical properties

We previously reported that cyclic voltammetry of **1aPd** showed a *pseudo*-reversible one-electron redox couple at +0.21 V vs a ferrocene/ferrocenium (Fc/Fc^+) standard in CH_2Cl_2 [83]. The one-electron oxidation of **1aPd** is accompanied by remarkable spectral changes in the Vis-NIR region; a red-shift of the major absorption band from $\lambda = 667$ nm to $\lambda = 767$ nm and development of a broad NIR band centered at $\lambda = 1408$ nm [83]. Having bimetallic helicates of hexapyrrole- α,ω -dicarbaldimines of high helical sense bias in hand, it is of great interest to investigate on their redox-triggered spectral changes in view of the recent progress in the chiroptical molecular switches [104-113].

One-electron oxidation of **2aPd**, **3aPd**, and **4aPd** occurred at by 0.05 ~ 0.08 V less positive potentials than that of **1aPd** (Table 2, ESI S24 and S25). Introduction of the 3,3'-dimethyl substituents at the 2,2'-bipyrrole subunit in the bisPd complexes caused positive shifts of $E_{1/2}$ by 0.03 ~ 0.09 V, which is ascribed to the less planar bisdipyrrin π -conjugated system of **1bPd** derivatives. As we previously reported [91], UV-vis and CD titration of **4aPd** in CH_2Cl_2 with AgClO_4 as an oxidizing agent almost completed at one molar equivalent (ESI S26, left). An ESR signal observed after AgClO_4 oxidation of **4aPd** is consistent with a π -cation radical species (ESI S10) [91]. In the course of this chemical oxidation, both the absorption band and the CD Cotton effect of **4aPd** at $\lambda = 699$ nm shifted to $\lambda = 741$ nm with isosbestic points. It is remarkable that the chiroptical properties of **4aPd** can be switched at moderately positive potential ($E_{1/2} = +0.14$ V vs Fc/Fc^+) with great changes in the CD intensity in the Vis-NIR region; $\Delta(\Delta\epsilon) = 150 \text{ M}^{-1}.\text{cm}^{-1}$ and $117 \text{ M}^{-1}.\text{cm}^{-1}$ at $\lambda = 699$ nm and 741 nm, respectively. Similar spectral changes of **3aNi** upon AgClO_4 oxidation are also recorded here (ESI S26, right). The Vis-NIR absorption band of **3aNi** at $\lambda = 711$ nm shifted to $\lambda = 758$ nm upon one-electron oxidation and its negative CD Cotton effect at $\lambda = 711$ nm shifted to $\lambda = 762$ nm with their CD intensity changes ($\Delta(\Delta\epsilon)$) of $116 \text{ M}^{-1}.\text{cm}^{-1}$ and $43 \text{ M}^{-1}.\text{cm}^{-1}$, respectively. In the present study, we have also found that the redox-triggered UV-vis-NIR absorption and CD changes of **4aPd** are alternatively reproduced upon electrolysis at the potential of +0.45 V (vs Ag/AgNO_3 reference electrode) followed by +0.20 V using a Pt mesh electrode (ESI S27). A very broad NIR absorption band ranging between 1000 nm and 1700 nm with a peak top at 1408 nm developed during electrooxidation of **4aPd**. This NIR band is very similar to that observed for the monocation of **1aPd** [83]. In the electrolysis of **4bPd** at +0.50 V, the UV-vis major band at $\lambda = 648$ nm decreased and two absorption bands at $\lambda = 655$ nm and 734 nm and a very broad NIR band ranging between 1000 nm and 2400 nm with a peak top at 1740 nm developed (Fig.11). The positive CD Cotton effect of **4bPd** at $\lambda = 644$ nm also decreased and two weaker signals at $\lambda = 661$ and 731 nm appeared in the cation radical state with their CD intensity ($\Delta\epsilon$) changed from +218 $\text{M}^{-1}.\text{cm}^{-1}$ to +43 $\text{M}^{-1}.\text{cm}^{-1}$ at 644 nm and from 0 $\text{M}^{-1}.\text{cm}^{-1}$ to +68 $\text{M}^{-1}.\text{cm}^{-1}$ at 731 nm. After one electrochemical redox cycle, the Vis-NIR absorbance and CD ellipticity of the major bands of **4bPd** recovered to 90% intensity of the original ones. This is less than 97% recovery of the major bands in the case of **4aPd**.

CONCLUSION

Bimetallic complexes of hexapyrrole- α,ω -dicarbaldimines with high helical sense bias were readily formed by using optically active amines as reagents for imine formation. The stereogenic center introduced at both ends of the oligopyrrole chain induced a strong CD 1st Cotton effect in the wavelength region around $\lambda = 700$ nm. These bimetallic complexes exist as a mixture of sigmoidal open forms and helical closed forms. Their composition depended on the metal, the amine source, and the hexapyrrole substituent. The ^1H NMR chemical shifts of the hexapyrrole ligand were successfully used to distinguish not only between a closed form and an open form in general but also between *P*-helix and *M*-helix in the special cases having N-[(*S*)-1-phenylethyl]carbaldimine parts. The stereochemistry was also confirmed by theoretical CD spectral simulation. BisPd complexes preferred a helical closed form and the methyl groups at the 3,3'-position of the 2,2'-bipyrrole subunit not only caused higher preference for a closed C_2 form to open forms but also improved helical sense bias between a pair of closed C_2 forms. Specifically, **4aPd** and **4bPd** having N-[(*R*)-(-)-1-cyclohexylethyl]carbaldimine parts adopted a *P*-helical closed form in 85% and 99% diastereoselectivity. In contrast, the bisNi complexes adopt a sigmoidal open form exclusively with a pair of Ni coordination sites being heterohelical. Although X-ray crystallography indicated mostly planar conformation of the bisdipyrrin π -conjugated unit of **4aNi** with N-[(*R*)-1-cyclohexylethyl]carbaldimine parts, the observed positive CD 1st Cotton effect at $\lambda = 712$ nm with a considerable strength suggested that a *P*-helical twist is induced on the

bisdipyrrin unit in solution. Their chiroptical properties are dependent on the conformation, that is, the intensity of the CD 1st Cotton effect ($\Delta\epsilon = 139 \text{ M}^{-1}.\text{cm}^{-1}$ at $\lambda = 712 \text{ nm}$) of **4aNi** is lower than that ($\Delta\epsilon = 208 \text{ M}^{-1}.\text{cm}^{-1}$ at $\lambda = 699 \text{ nm}$) of **4aPd**, while the intensity of the major Vis-NIR absorption band ($\epsilon = 134000 \text{ M}^{-1}.\text{cm}^{-1}$ at $\lambda = 715 \text{ nm}$) of **4aNi** is twice as large as that ($\epsilon = 59400 \text{ M}^{-1}.\text{cm}^{-1}$ at $\lambda = 702 \text{ nm}$) of **4aPd**. Spectroelectrochemistry showed that a stable π -cation radical was generated reversibly at potentials of +0.1~0.3 V vs a Fc/Fc^+ couple resulting in remarkable spectral changes in the Vis-NIR region. The observed switching ranges of the molar circular dichroic absorption ($\Delta(\Delta\epsilon) = 150 \text{ M}^{-1}.\text{cm}^{-1}$ at $\lambda = 699 \text{ nm}$ and $\Delta(\Delta\epsilon) = 117 \text{ M}^{-1}.\text{cm}^{-1}$ at $\lambda = 741 \text{ nm}$) in the case of **4aPd** are remarkable in the Vis-NIR region. It is of importance that compounds showing redox activity at moderately positive potentials and chiroptical properties in the Vis-NIR region are available without optical resolution procedure. Screening of the amine sources for desired chiroptical properties and introducing additional functionalities can be done quite easily. The present helicates are regarded as a scaffold for generating unique optoelectronic functional materials.

EXPERIMENTAL

General

^1H and ^{13}C NMR spectra were recorded on a Varian Inova 400 spectrometer (400 MHz) and Bruker Ascend 400 (400 MHz). Chemical shifts were referenced with respect to $(\text{CH}_3)_4\text{Si}$ (0 ppm) as an internal standard. The UV-vis-NIR and CD spectra were measured on a JASCO V-670 spectrometer and JASCO J-820F spectropolarimeter, respectively. Elemental analyses of C, H, and N were made with a YANACO MT-5 CHN recorder. ESITOF-MS spectra were measured with an Applied Biosystems Mariner mass spectrometer and TQ Orbitrap Discovery (Thermo Fisher Scientific). FAB-MS spectra were measured with JEOL LCmate using 3-nitrobenzyl alcohol as a matrix. Cyclic voltammetric analysis was performed using ALS/CHI-606S voltammetric analyzer using glassy carbon as a working electrode, platinum wire as a counter electrode, and an Ag/AgNO_3 reference electrode.

Bruker Apex-II diffractometer equipped with a CCD detector was used for data collection of the X-ray crystallography. An empirical absorption correction was applied using the SADABS program. The structure was solved by the direct method and refined by full-matrix least-squares calculations on F^2 using the Shelxtl 97 program package [114].

In the theoretical study, initial geometries for structure optimization were created using atom coordinates of the hexapyrrole core revealed by X-ray crystallography (**4aPd** for a closed form and **4aNi** for a heterohelical open form). All structures were fully optimized without any symmetry constraint. The calculations were performed by the density functional theory (DFT) method with a ωB97XD functional, employing a basis set consisting of LANL2DZ for Ni, Pd and 6-31G(d) for C, H, N. All the calculations were performed using the Gaussian 09 program [115]. Theoretically optimized models of **3aNi** and **4aNi** (in heterohelical open forms) and of **3aPd**, **3bPd**, **4aPd**, and **4bPd** (in a closed form) shown in ESI S13, S14, S16, and S17 were subjected to TDDFT calculation on the $\omega\text{B97XD}/(6\text{-}31\text{G}(\text{d}))$ for C,H,N and LANL2DZ for Ni, Pd) level using the Gaussian 09 program. The resulting theoretical spectra (ESI S22 and S23) were drawn using Gausssum ver.2.2 [116].

Cyclic voltammetric analysis was performed using ALS/CHI-606S voltammetric analyzer using glassy carbon as a working electrode, platinum wire as a counter electrode, and an Ag/AgNO_3 reference electrode. A quartz cuvette of 1.0 mm sample length equipped with a platinum mesh working electrode, a platinum wire counter electrode, and an Ag/AgNO_3 reference electrode was used for spectroelectrochemistry.

Biscopper(II) complexes of hexapyrrole- α,ω -di-N-alkylcarbaldimines 2aCu, 3aCu, and 4aCu

A dry THF solution (10 mL) of **1aCu** (23.6 mg) and alkylamine (benzylamine, (*S*)-(-)-1-phenylethylamine, and (*R*)-(-)-1-cyclohexylethylamine) (20 mL) was refluxed with stirring for 4 h. The color of the solution turned from green to blue. After the solvent was removed under vacuum, column chromatography on alumina (Activity II) with CH₂Cl₂ as eluent gave a blue fraction. Recrystallization from CH₂Cl₂-MeOH afforded black powders. **2aCu** (from benzylamine): Yield 93%. UV-vis (CH₂Cl₂): $\lambda_{\max}$, nm (log ϵ) 347 (4.66), 491 (3.85), 649 (sh, 4.59), 709 (5.04). ESI-MS: m/z 1093.37 (calcd. for C₆₆H₆₂N₈Cu₂ + H⁺ 1093.38). Anal. calcd. for C₆₆H₆₂N₈Cu₂: C, 72.44; H, 5.71; N, 10.24%. Found: C, 72.17; H, 5.51; N, 10.28.

3aCu (from (*S*)-(-)-1-phenylethylamine): Yield 56%. UV-vis (CH₂Cl₂): $\lambda_{\max}$, nm (log ϵ) 346 (4.62), 491 (3.77), 646 (sh, 4.57), 703 (5.00). CD (CH₂Cl₂): $\lambda_{\max}$, nm ($\Delta\epsilon$, M⁻¹.cm⁻¹) 342 (-17.9), 409 (8.1), 495 (44.7), 637 (-32.4), 694 (-72.1). ESI-MS: m/z 1121.40 (calcd. for C₆₈H₆₆N₈Cu₂ + H⁺ 1121.41). Anal. calcd. for C₆₈H₆₆N₈Cu₂•(H₂O)₂: C, 70.50; H, 6.09; N, 9.67%. Found: C, 70.91; H, 5.84; N, 9.64.

4aCu (from (*R*)-(-)-1-cyclohexylethylamine): Yield 72%. UV-vis (CH₂Cl₂): $\lambda_{\max}$, nm (log ϵ) 344 (4.60), 491 (3.83), 645 (sh, 4.57), 705 (5.02). CD (CH₂Cl₂): $\lambda_{\max}$, nm ($\Delta\epsilon$, M⁻¹.cm⁻¹) 342 (10.5), 487 (-37.1), 648 (18.5), 706 (55.2). ESI-MS: m/z 1133.50 (calcd. for C₆₈H₇₈N₈Cu₂ + H⁺ 1133.50). Anal. calcd. for C₆₈H₇₈N₈Cu₂•(H₂O)₂: C, 69.77; H, 7.06; N, 9.57%. Found: C, 69.98; H, 6.73; N, 9.57.

Bisnickel(II) complexes of hexapyrrole- α,ω -di-*N*-alkylcarbaldimines 2aNi, 3aNi, and 4aNi

A mixture of **1aNi** (10 mg, 0.01 mmol), alkylamine (benzylamine, (*S*)-(-)-1-phenylethylamine, and (*R*)-(-)-1-cyclohexylethylamine) (80 mL), toluene (3 mL), and ethanol (1 mL) for 24 h at reflux. The color of the solution turned from green to blue. After the solvent was removed under vacuum, column chromatography on alumina with CH₂Cl₂ as eluent gave a blue fraction. Recrystallization from CH₂Cl₂-MeOH afforded black powders. **2aNi** (from benzylamine): Yield 95%. ¹H NMR (400 MHz, δ -value, in CDCl₃) 9.89 (s, 2H, bipyrrole-3,3'-*H*); 7.47~7.18 (m, 20H, *meso*-Ph-*H* and N-benzyl-Ph-*H*); 6.99 (s, 2H, N=CH); 6.48, 6.30 (d $\times$ 2, 2H $\times$ 2, *J* = 4.3 Hz, pyrrole- β -*H*); 6.47, 5.98 (d $\times$ 2, 2H $\times$ 2, *J* = 3.7 Hz, formimidoylpyrrole- β -*H*); 3.60, 3.54 (d $\times$ 2, 2H $\times$ 2, *J* = 14.6 Hz, N-CH₂Ph); 1.83, 1.65 (s $\times$ 2, 6H $\times$ 2, CMe₂); 1.58 (m, 2H, CH₂CH₂CH₃); 1.25 (m, 4H, CH₂CH₂CH₃); 1.12 (m, 2H, CH₂CH₂CH₃); 0.59 (t, 6H, *J* = 7.1 Hz, CH₂CH₂CH₃). ¹³C NMR (100 MHz, δ -value, in CDCl₃) 168.83, 159.17, 156.00, 151.70, 148.99, 142.92, 139.25, 138.40, 138.08, 137.47, 136.95, 130.58, 129.91, 129.30, 128.15, 128.05, 127.89, 127.77, 127.50, 126.70, 121.50, 115.17, 114.42, 105.16, 58.89, 39.76, 36.82, 30.46, 24.34, 22.41, 13.84. UV-vis (CH₂Cl₂): $\lambda_{\max}$, nm (log ϵ) 344 (4.50), 389 (sh, 4.30), 498 (3.90), 653 (4.54), 717 (5.08). FAB-MS: m/z 1082.4 (calcd. for C₆₆H₆₂N₈Ni₂⁺ 1082.4). Anal. calcd. for C₆₆H₆₂N₈Ni₂•(H₂O)_{0.5}: C, 72.48; H, 5.81; N, 10.25%. Found: C, 72.33; H, 5.77; N, 10.23.

3aNi (from (*S*)-(-)-1-phenylethylamine): Yield 83%. ¹H NMR (400 MHz, δ -value, in CDCl₃) 10.75, 8.76 (s $\times$ 2, 1H $\times$ 2, bipyrrole-3,3'-*H*); 7.68 (d, 1H, *J* = 6.8 Hz, *meso*-Ph-*o*-*H*); 7.56~7.28 (m, 10H, *meso*-Ph-*H* and N-benzyl-Ph-*H*); 7.39, 6.26 (s $\times$ 2, 1H $\times$ 2, N=CH); 7.14, 6.48 (d $\times$ 2, 2H $\times$ 2, *J* = 7.0, 7.3 Hz, N-benzyl-Ph-*o*-*H*); 7.06 (t, 1H, *J* = 7.3 Hz, N-benzyl-Ph-*p*-*H*); 7.01 (d, 2H, *J* = 7.8 Hz, *meso*-Ph-*o*-*H*); 6.87 (t, 2H, *J* = 7.7 Hz, N-benzyl-Ph-*m*-*H*); 6.63, 6.37 (d $\times$ 2, 1H $\times$ 2, *J* = 4.2 Hz, pyrrole- β -*H*); 6.56, 5.95 (d $\times$ 2, 1H $\times$ 2, *J* = 3.6 Hz, formimidoylpyrrole- β -*H*); 6.49, 6.21 (d $\times$ 2, 1H $\times$ 2, *J* = 4.0 Hz, pyrrole- β -*H*); 6.20, 5.88 (d $\times$ 2, 1H $\times$ 2, *J* = 3.7 Hz, formimidoylpyrrole- β -*H*); 4.04, 3.82 (q $\times$ 2, 1H $\times$ 2, *J* = 6.7 Hz, N-CHMePh); 1.84, 1.37 (s $\times$ 2, 3H $\times$ 2, CMe₂-axial-CH₃); 1.66, 1.54 (s $\times$ 2, 3H $\times$ 2, CMe₂-equatorial-CH₃); 1.41, 1.18 (d $\times$ 2, 3H $\times$ 2, *J* = 6.8 Hz, N-CHCH₃Ph); 1.9~0.9 (m, 8H, CH₂CH₂CH₃); 0.60, 0.51 (t $\times$ 2, 3H $\times$ 2, *J* = 7.3 Hz, CH₂CH₂CH₃). ¹³C NMR (100 MHz, δ -value, in CDCl₃) 169.70, 169.28, 157.07, 155.50, 155.13, 154.39, 151.40, 150.15, 149.97, 148.53, 143.95, 143.34, 142.73, 139.58, 139.05, 139.04, 138.60, 137.96, 137.84, 137.58, 137.56, 137.43, 131.33, 130.88, 130.00, 129.93, 129.39, 129.36, 128.88,

128.30, 128.30 (broad), 128.11, 128.07, 128.02, 127.68, 127.62, 127.46, 127.40, 126.64, 126.56, 123.34, 120.04, 115.08, 114.92, 114.83, 114.37, 105.14, 104.62, 60.18, 59.90, 39.97, 39.65, 36.79, 36.63, 30.70, 30.63, 24.83, 23.95, 23.76, 22.21, 22.05, 21.68, 13.94, 13.86. UV-vis (CH_2Cl_2): λ_{max} , nm (log ϵ) 345 (4.51), 386 (sh, 4.30), 497 (3.90), 652 (4.52), 712 (5.04). CD (CH_2Cl_2): λ_{max} , nm ($\Delta\epsilon$, $\text{M}^{-1}\cdot\text{cm}^{-1}$) 457 (50.6), 521 (31.1), 647 (−43.8), 709 (−137.8). ESI-MS: m/z 1111.40 (calcd. for $\text{C}_{68}\text{H}_{66}\text{N}_8\text{Ni}_2 + \text{H}^+$ 1111.42). Anal. calcd. for $\text{C}_{68}\text{H}_{66}\text{N}_8\text{Ni}_2$: C, 73.40; H, 5.98; N, 10.07%. Found: C, 73.41; H, 6.08; N, 10.18.

4aNi (from (*R*)-(−)-1-cyclohexylethylamine): Yield 80%. ^1H NMR (400 MHz, δ -value, in CDCl_3) 10.80, 9.06 (s×2, 1H×2, bipyrrole-3,3'-*H*); 7.64, 7.60, 7.28, 7.20 (d×4, 1H×4, $J = 6.8\sim 7.7$ Hz, *meso*-Ph-*o*-*H*); 7.52~7.38 (m, 6H, *meso*-Ph-*H*); 6.99, 6.79 (s×2, 1H×2, N=CH); 6.54, 6.52, 6.31, 6.27, (d×4, 1H×4, $J = 4.2$ Hz, pyrrole- β -*H*); 6.42, 6.33, 5.94, 5.90 (d×4, 1H×4, $J = 3.6$ Hz, pyrrole- β -*H*); 2.38, 2.04 (m×2, 1H×2, N-CHMe-cyclohexyl); 1.13, 0.70 (d×2, 3H×2, $J = 6.4, 6.7$ Hz, N-CHCH₃-cyclohexyl); 1.89, 1.77 (s×2, 3H×2, CMe₂-axial-CH₃); 1.65, 1.63 (s×2, 3H×2, CMe₂-equatorial-CH₃); 1.9~0.8 (m, CH₂CH₂CH₃ and cyclohexyl-*H*); 0.62, 0.59 (t×2, 3H×2, $J = 7.3$ Hz, CH₂CH₂CH₃); 0.26, −0.37 (q×2, 1H×2, $J = 12.9$ Hz, cyclohexyl-axial-*H*). ^{13}C NMR (100 MHz, δ -value, in CDCl_3) 169.88, 168.55, 157.24, 155.44, 155.09, 154.74, 150.65, 150.19, 150.10, 148.58, 143.20, 142.28, 139.52, 139.26, 139.05, 138.56, 138.30, 138.12, 137.80, 137.57, 131.02, 130.43, 129.87, 129.76, 129.30, 129.24, 128.27, 128.18, 128.12, 127.89, 127.72, 127.61, 122.94, 120.43, 114.70, 114.24, 113.96, 113.79, 104.42, 104.33, 61.53, 59.58, 44.43, 39.71, 39.68, 36.77, 31.27, 30.75, 30.69, 29.96, 28.23, 27.10, 26.84, 26.78, 26.61, 26.50, 26.22, 25.42, 24.37, 24.29, 23.69, 22.35, 21.51, 14.48, 13.82, 13.80. UV-vis (CH_2Cl_2): λ_{max} , nm (log ϵ) 344 (4.51), 386 (sh, 4.29), 501 (3.90), 652 (4.54), 715 (5.12). CD (CH_2Cl_2): λ_{max} , nm ($\Delta\epsilon$, $\text{M}^{-1}\cdot\text{cm}^{-1}$) 457 (−42.7), 514 (−28.1), 650 (34.8), 712 (139.3). ESI-MS: m/z 1223.50 (calcd. for $\text{C}_{68}\text{H}_{78}\text{N}_8\text{Ni}_2 + \text{H}^+$ 1223.51). Anal. calcd. for $\text{C}_{68}\text{H}_{78}\text{N}_8\text{Ni}_2$: C, 72.61; H, 6.99; N, 9.96%. Found: C, 72.29; H, 7.09; N, 9.90.

Bispalladium(II) complexes of hexapyrrole- α,ω -di-*N*-alkylcarbaldimines 2aPd, 3aPd, and 4aPd

A mixture of **1aPd** (10 mg, 0.01 mmol), alkylamine (benzylamine, (*S*)-(−)-1-phenylethylamine, and (*R*)-(−)-1-cyclohexylethylamine) (80 μL) and CHCl_3 (5 mL) was stirred for 5 h at reflux. The color of the solution turned dark green. After the solvent was removed under vacuum, column chromatography on alumina with CH_2Cl_2 as an eluent gave a green fraction. Recrystallization from CH_2Cl_2 -MeOH afforded green powders. **2aPd** (from benzylamine): Yield 85%. ^1H NMR of the major conformer (400 MHz, δ -value, in CDCl_3) 7.02 (s, 2H, N=CH); 7.6~6.8 (m, 20H, *meso*-Ph-*H* and N-benzyl-Ph-*H*); 6.58 (s, 2H, bipyrrole-3,3'-*H*); 6.43, 6.34 (d×2, 2H×2, $J = 4.4$ Hz, pyrrole- β -*H*); 6.32, 5.85 (d×2, 2H×2, $J = 3.8$ Hz, formimidoylpyrrole- β -*H*); 3.55, 3.50 (d×2, 2H×2, $J = 15.1$ Hz, N-CH₂Ph); 1.64, 0.85 (s×2, 6H×2, CMe₂); 1.45 (m, 4H, CH₂CH₂CH₃); 1.22 (sextet, 4H, $J = 7.3$ Hz, CH₂CH₂CH₃); 0.56 (t, 6H, $J = 7.3$ Hz, CH₂CH₂CH₃). ^{13}C NMR of the major conformer (100 MHz, δ -value, in CDCl_3) 167.04, 160.50, 153.64, 148.41, 147.70, 143.81, 139.26, 138.94, 138.20, 136.40, 136.35, 130.47, 130.11, 129.71, 128.07, 127.96, 127.92, 127.70, 127.34, 126.51, 124.73, 115.72, 114.75, 105.36, 59.63, 40.96, 34.16, 31.23, 26.01, 24.55, 14.04. UV-vis (CH_2Cl_2): λ_{max} , nm (log ϵ) 368 (sh, 4.46), 418 (sh, 4.20), 487 (4.29), 643 (sh, 4.34), 701 (4.85). ESI-MS: m/z 1181.31 (calcd. for $\text{C}_{66}\text{H}_{62}\text{N}_8\text{Pd}_2^+$ 1181.32). Anal. calcd. for $\text{C}_{66}\text{H}_{62}\text{N}_8\text{Pd}_2$: C, 67.17; H, 5.30; N, 9.50%. Found: C, 66.91; H, 5.46; N, 9.53.

3aPd (from (*S*)-(−)-1-phenylethylamine): Yield 59%. ^1H NMR of the major conformer (400 MHz, δ -value, in CDCl_3) 7.34 (s, 2H, N=CH); 7.7~6.9 (m, 20H, *meso*-Ph-*H* and N-benzyl-Ph-*H*); 6.85 (s, 2H, bipyrrole-3,3'-*H*); 6.40, 6.28 (d×2, 2H×2, $J = 4.4$ Hz, pyrrole- β -*H*); 6.36, 5.84 (d×2, 2H×2, $J = 3.8$ Hz, formimidoylpyrrole- β -*H*); 4.02 (q, 2H, $J = 6.6$ Hz, N-CHMePh); 1.62, 0.86 (s×2, 6H×2, CMe₂); 1.6~1.2 (m, 8H, CH₂CH₂CH₃); 1.12 (d, 6H, $J = 6.6$ Hz, N-CHCH₃Ph); 0.62 (t, 6H, $J = 7.1$ Hz, CH₂CH₂CH₃). UV-vis (CH_2Cl_2): λ_{max} , nm (log ϵ) 368 (sh, 4.45), 420 (sh, 4.13), 488 (4.23), 643 (sh, 4.37), 701

(4.88). CD (CH_2Cl_2): λ_{max} , nm ($\Delta\epsilon$, $\text{M}^{-1}\cdot\text{cm}^{-1}$) 425 (11.4), 477 (16.6), 519 (−22.9), 689 (−40.2). ESI-MS: m/z 1209.35 (calcd. for $\text{C}_{68}\text{H}_{66}\text{N}_8\text{Pd}_2 + \text{H}^+$ 1209.35). Anal. calcd. for $\text{C}_{68}\text{H}_{66}\text{N}_8\text{Pd}_2\cdot(\text{H}_2\text{O})$: C, 66.61; H, 5.59; N, 9.14%. Found: C, 66.62; H, 5.61; N, 9.02.

4aPd (from (*R*)-(−)-1-cyclohexylethylamine): Yield 80%. ^1H NMR of the major conformer (400 MHz, δ -value, in CDCl_3) 7.10 (s, 2H, N=CH); 7.5~7.2 (m, 10H, *meso*-Ph-*H*); 6.80 (s, 2H, bipyrrrole-3,3'-*H*); 6.41, 6.27 (d $\times$ 2, 2H $\times$ 2, J = 4.4 Hz, pyrrole- β -*H*); 6.30, 5.84 (d $\times$ 2, 2H $\times$ 2, J = 3.6 Hz, formimidoylpyrrole- β -*H*); 2.66 (quintet, 2H, J = 6.6 Hz, N-CHMe-cyclohexyl); 1.93 (d, 2H, J = 12.8 Hz, cyclohexyl-equatorial-*H*); 1.64, 0.87 (s $\times$ 2, 6H $\times$ 2, CMe_2); 1.65~1.4, 1.4~1.2, 1.1~0.9, 0.75~0.65 (m, 26H, $\text{CH}_2\text{CH}_2\text{CH}_3$ and cyclohexyl-*H*); 0.69 (d, 6H, J = 6.7 Hz, N-CHCH $_3$ -cyclohexyl); 0.61 (t, 6H, J = 7.3 Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$); 0.46 (q, 2H, J = 11.0 Hz, cyclohexyl-axial-*H*). ^{13}C NMR of the major conformer (100 MHz, δ -value, in CDCl_3) 167.29, 156.49, 153.54, 148.16, 147.52, 143.36, 139.37, 138.58, 137.55, 127.25, 130.39, 130.02, 129.32, 127.78, 127.67, 127.30, 124.74, 114.57, 114.43, 104.80, 60.52, 46.21, 40.82, 34.09, 31.32, 29.89, 28.44, 26.39, 26.31, 26.20, 25.65, 24.73, 16.37, 14.05. UV-vis (CH_2Cl_2): λ_{max} , nm (log ϵ) 368 (sh, 4.43), 417 (4.28), 484 (4.38), 645 (sh, 4.29), 702 (4.77). CD (CH_2Cl_2): λ_{max} , nm ($\Delta\epsilon$, $\text{M}^{-1}\cdot\text{cm}^{-1}$) 367 (−39.7), 426 (−59.0), 482 (−79.2), 646 (82.5), 699 (207.8). ESI-MS: m/z 1221.44 (calcd. for $\text{C}_{68}\text{H}_{78}\text{N}_8\text{Pd}_2 + \text{H}^+$ 1221.44). Anal. calcd. for $\text{C}_{68}\text{H}_{78}\text{N}_8\text{Pd}_2$: C, 66.93; H, 6.44; N, 9.18%. Found: C, 67.08; H, 6.66; N, 9.22.

Bispalladium(II) complexes of hexapyrrole- α,ω -di-*N*-alkylcarbaldimines 2bPd, 3bPd, and 4bPd

A mixture of **1bPd** (20 mg, 0.02 mmol), alkylamine (benzylamine, (*S*)-(−)-1-phenylethylamine, and (*R*)-(−)-1-cyclohexylethylamine) (80 μL) and dry THF (5 mL) was stirred for 5 h at reflux. The color of the solution turned dark green. After the solvent was removed under vacuum, column chromatography on alumina with CH_2Cl_2 as eluent gave a green fraction. Recrystallization from CH_2Cl_2 -MeOH afforded brown powders. **2bPd** (from benzylamine): Yield 76%. ^1H NMR of the major conformer (400 MHz, δ -value, in CDCl_3) 7.65~7.42 (m, 10H, *meso*-Ph-*H*); 7.22~7.15 (m, 6H, N-benzyl-Ph-*m,p*-*H*); 6.97 (m, 4H, N-benzyl-Ph-*o*-*H*); 6.87 (s, 2H, N=CH); 6.57, 6.43 (d $\times$ 2, 2H $\times$ 2, J = 4.4 Hz, pyrrole- β -*H*); 6.22, 5.80 (d $\times$ 2, 2H $\times$ 2, J = 3.8 Hz, formimidoylpyrrole- β -*H*); 3.89, 3.29 (d $\times$ 2, 2H $\times$ 2, J = 14.9 Hz, N-CH $_2$ Ph); 1.78 (s, 6H, bipyrrrole-3,3'-CH $_3$); 1.61, 0.93 (s $\times$ 2, 6H $\times$ 2, CMe_2); 1.73, 1.42 (m $\times$ 2, 2H $\times$ 2, bipyrrrole-4,4'-CH $_2\text{CH}_3$); 0.67 (t, 6H, J = 7.2 Hz, bipyrrrole-4,4'-CH $_2\text{CH}_3$). ^{13}C NMR of the major conformer (100 MHz, δ -value, in CDCl_3) 169.48, 160.23, 153.18, 149.44, 145.25, 145.04, 139.65, 139.21, 139.16, 136.99, 134.03, 130.92, 130.90, 130.85, 130.51, 129.14, 128.45, 128.32, 127.66, 127.13, 126.93, 115.36, 114.88, 105.13, 60.08, 40.70, 34.20, 25.61, 20.10, 15.40, 12.46. UV-vis (CH_2Cl_2): λ_{max} , nm (log ϵ) 371 (sh, 4.56), 435 (sh, 4.27), 501 (4.56), 654 (4.74). ESI-MS: m/z 1180.32 (calcd. for $\text{C}_{66}\text{H}_{62}\text{N}_8\text{Pd}_2^+$ 1180.32). Anal. calcd. for $\text{C}_{66}\text{H}_{62}\text{N}_8\text{Pd}_2\cdot(\text{CH}_2\text{Cl}_2)_{1.4}$: C, 62.32; H, 5.03; N, 8.63%. Found: C, 62.42; H, 5.10; N, 8.64.

3bPd (from (*S*)-(−)-1-phenylethylamine): Yield 78%. ^1H NMR of the major conformer (400 MHz, δ -value, in CDCl_3) 7.58~7.39 (m, 10H, *meso*-Ph-*H*); 7.24~7.16 (m, 6H, N-benzyl-Ph-*m,p*-*H*); 6.83 (br, 4H, N-benzyl-Ph-*o*-*H*); 6.67, 6.44 (d $\times$ 2, 2H $\times$ 2, J = 4.3 Hz, pyrrole- β -*H*); 6.47 (s, 2H, N=CH); 6.15, 5.77 (d $\times$ 2, 2H $\times$ 2, J = 3.8 Hz, formimidoylpyrrole- β -*H*); 3.97 (q, 2H, J = 6.5 Hz, N-CHMePh); 1.76 (s, 6H, bipyrrrole-3,3'-CH $_3$); 1.60, 1.02 (s $\times$ 2, 6H $\times$ 2, CMe_2); 1.48, 1.32 (m $\times$ 2, 2H $\times$ 2, bipyrrrole-4,4'-CH $_2\text{CH}_3$); 1.30 (d, 6H, J = 6.8 Hz, N-CHCH $_3$ Ph); 0.33 (t, 6H, J = 7.4 Hz, 4,4'-CH $_2\text{CH}_3$). ^{13}C NMR of the major conformer (100 MHz, δ -value, in CDCl_3) 170.15, 157.68, 152.78, 149.52, 145.82, 145.19, 140.45, 139.69, 139.50, 137.24, 134.39, 131.09, 131.02, 130.90, 130.36, 129.5 (broad), 128.36, 128.14, 127.70, 127.19, 126.96, 115.10, 115.05, 104.82, 61.25, 40.51, 34.00, 25.12, 21.44, 20.22, 14.26, 12.23. UV-vis (CH_2Cl_2): λ_{max} , nm (log ϵ) 372 (sh, 4.39), 432 (sh,

4.14), 509 (4.41), 651 (4.52). CD (CH₂Cl₂): λ_{max} , nm ($\Delta\epsilon$, M⁻¹.cm⁻¹) 362 (−30.4), 404 (5.8), 510 (−135.1), 650 (233.9). ESI-MS: m/z 1208.35 (calcd. for C₆₈H₆₆N₈Pd₂⁺ 1208.35). Anal. calcd. for C₆₈H₆₆N₈Pd₂•(CH₂Cl₂): C, 64.09; H, 5.30; N, 8.67%. Found: C, 64.12; H, 5.37; N, 8.70.

4bPd (from (*R*)-(−)-1-cyclohexylethylamine): Yield 83%. ¹H NMR (400 MHz, δ -value, in CDCl₃) 7.45~7.32 (m, 10H, *meso*-Ph-*H*); 7.07 (s, 2H, N=CH); 6.46, 6.40 (d×2, 2H×2, J = 4.3 Hz, pyrrole- β -*H*); 6.28, 5.83 (d×2, 2H×2, J = 3.8 Hz, formimidoylpyrrole- β -*H*); 2.68 (quintet, 2H, J = 6.3 Hz, N-CHMe-cyclohexyl); 2.34 (d, 2H, J = 12.3 Hz, cyclohexyl-equatorial-*H*); 1.90 (s, 6H, bipyrrole-3,3'-CH₃); 1.70, 1.53 (m×2, 2H×2, bipyrrole-4,4'-CH₂CH₃); 1.62, 0.94 (s×2, 6H×2, CMe₂); 1.62~1.52, 1.34~1.26, 1.12~0.94, 0.60~0.53 (m, 20H, cyclohexyl-*H*); 0.70 (t, 6H, J = 7.3 Hz, bipyrrole-4,4'-CH₂CH₃); 0.53 (d, 6H, J = 6.8 Hz, N-CHCH₃-cyclohexyl). ¹³C NMR (100 MHz, δ -value, in CDCl₃) 169.01, 156.84, 152.67, 148.68, 145.54, 144.68, 139.86, 139.30, 137.62, 134.45, 130.52, 130.25, 130.15, 129.80, 128.08, 127.57, 126.98, 114.44, 114.23, 104.75, 62.20, 47.84, 40.64, 34.10, 30.31, 29.80, 26.68, 26.55, 26.30, 25.50, 20.32, 16.97, 15.08, 13.16. UV-vis (CH₂Cl₂): λ_{max} , nm (log ϵ) 371 (sh, 4.40), 435 (sh, 4.14), 495 (4.41), 648 (4.61). CD (CH₂Cl₂): λ_{max} , nm ($\Delta\epsilon$, M⁻¹.cm⁻¹) 362 (31.8), 403 (8.4), 494 (−110.0), 646 (217.7). ESI-MS: m/z 1220.44 (calcd. for C₆₈H₇₈N₈Pd₂⁺ 1220.44). Anal. calcd. for C₆₈H₇₈N₈Pd₂•(H₂O)_{1.5}: C, 65.48; H, 6.54; N, 8.98%. Found: C, 65.65; H, 6.38; N, 8.79.

Supporting Information

A full list of additional Figures and Tables (ESI S1~S27) are given in the supplementary material. This material available at <http://www.u-bourgogne.fr/jpp/>.

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NOTES AND REFERENCES

† Atom numbering scheme of **3aNi** begins with the hexapyrrole core (1~30), and then proceeds to the peripheral substituents (31~52), and the N-alkyl groups (53~68). Small atom numbers (the Ni atom (1), the nitrogen atoms (1~4), the hexapyrrole core (1~15), the peripheral substituents (31~41), and the N-alkyl groups (53~60)) are allocated to the *M*-helical coordination site, and big atom numbers (the Ni atom (2), the nitrogen atoms (5~8), the hexapyrrole core (16~30), the peripheral substituents (42~52), and the N-alkyl groups (61~68)) to the *P*-helical coordination site of **3aNi** (Fig. 2). In contrast, small atom numbers are allocated to the *P*-helical coordination site of **4aNi** (Fig. 3 and ESI S1) because the (*R,P*) stereochemistry of **4aNi** has a similar atom arrangement to the (*S,M*) stereochemistry of **3aNi**. A similar atom numbering scheme is used in **3aPd**, **4aPd**, **3bPd**, and **4bPd** (Fig. 6, 7, 8, and Scheme 4).

§ CCDC deposition numbers 2069208 (**4aNi**), 898176 (**2aPd**), 2069209 (**2bPd**), and 898177 (**4aPd**) contain the supplementary crystallographic data for this paper. We already reported those data of **2aPd** and **4aPd** in our preliminary communication [91]. These data are provided free of charge by the joint Cambridge Crystallographic Data Center and Fachinformationszentrum Karlsruhe Access Structures service via www.ccdc.cam.ac.uk/structures.

∞ The distances in the DFT-optimized (*M,P,P*)-model of **4aNi** are 2.34 Å for H14–Ni2 and 2.76 Å for H17–Ni1 (ESI S14).

- ‡ Since three singlets at $\delta = 1.85, 1.78$ and 1.74 ppm due to the methyl protons of the *gem*-dimethylmethylene bridge are of equal integral in the ^1H NMR of **2aPd**, two singlets due to two methyl protons of the major open form appear at discrete chemical shifts and singlets due to two methyl protons of the minor open form are overlapped.
- ¶ Distances (Å) of short contact between the methyl protons (H32 and H52) of the *gem*-dimethylmethylene bridge and the formimidoylpyrrole groups of the opposite side in the X-ray structures of **2aPd** [2.64 (H32-N7), 2.76 (H32-C29), 2.78 (H52-N2)], **2bPd** [2.72 (H32-N7), 2.80 (H52-N2)], and **4aPd** [2.71 (H32-N7), 2.81 (H32-C29), 2.70 (H52-N2) 2.78 (H52-C2)].
- # Distances (Å) of short contact between the 2,2'-bipyrrole subunit and the N-alkyl protons of **2aPd** [2.68 (H53-N5), 2.54 (H53-C16), 2.75 (H60-N4), 2.47 (H60-C15)], **2bPd** [2.68 (H53'-N5), 2.62 (H53'-C16), 2.70 (H53'-C17), 2.80 (H53'-C19), 2.79 (H53-C16), 2.76 (H60'-N4), 2.66 (H60'-C15), 2.70 (H60'-C14), 2.75 (H60-C15)], and **4aPd** [2.65 (H53-C15), 2.48 (H53-C16), 2.78 (H57-C12), 2.77 (H61-C14), 2.37 (H61-C15), 2.70 Å (H61-C16)].
- ** Distances (Å) between the benzyl phenyl atoms and the pyrrole atoms of **2aPd**: 3.43 (C54-N4), 3.26 (C54-C15), 3.57 (C55-C15), 3.55 (C59-C12), 3.36 (C59-N4), 3.48 (C61-N5), 3.52 (C61-C16), 3.47 (C62-C16), 3.59 (C62-C17).

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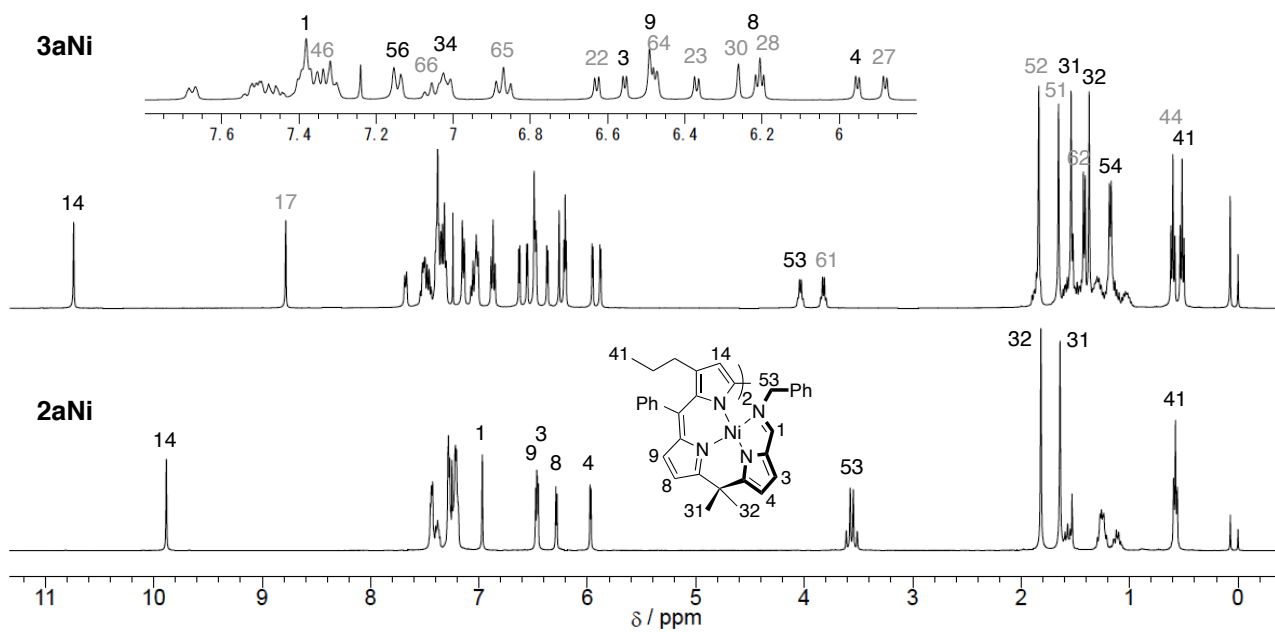


Fig. 1. ^1H NMR spectra of **2aNi** (bottom) and **3aNi** (top) in CDCl_3 . See an atom numbering scheme of **3aNi** in Fig. 2.

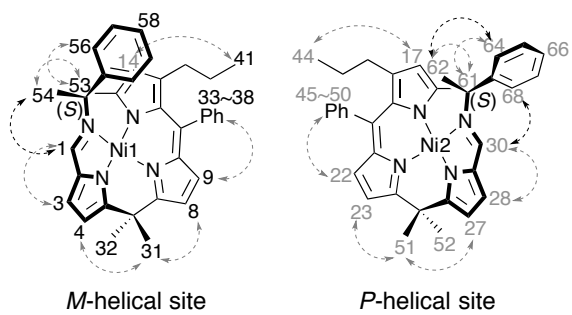


Fig. 2. Nickel coordination sites of **3aNi** with selected ^1H - ^1H NOESY correlations (ESI S2~S4) indicated by double-headed arrows.

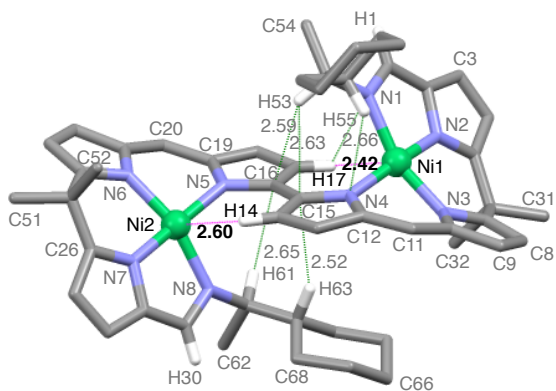


Fig. 3. X-ray diagram of **4aNi** with distances (Å) of short contact: 2.42 (H17–Ni1), 2.60 (H14–Ni2), 2.65 (H61–C16), 2.52 (H63–C15), 2.59 (H53–C16), 2.63 (H53–C15), and 2.66 (H55–N4). Propyl groups at C13 and C18 and phenyl groups at C11 and C20 were omitted for clarity.

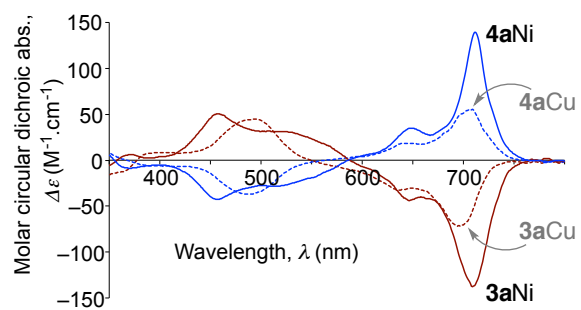


Fig. 4. CD spectra of bisCu complexes (**3aCu**, **4aCu**; broken lines) and bisNi complexes (**3aNi**, **4aNi**; solid lines) in CH_2Cl_2 .

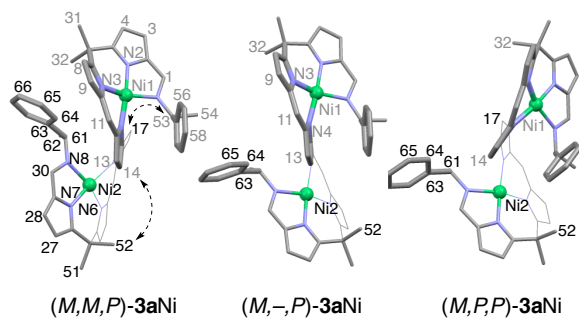


Fig. 5. Theoretically optimized structures of *(M,M,P)*- *(M,-,P)*- and *(M,P,P)*-open forms of **3aNi** in their side views with peripheral phenyl and propyl groups are omitted for clarity. Short distances of 2.33 Å (H53–H17) and 2.50 Å (H14–H52) in the *(M,M,P)*-model are indicated by double-headed arrows.

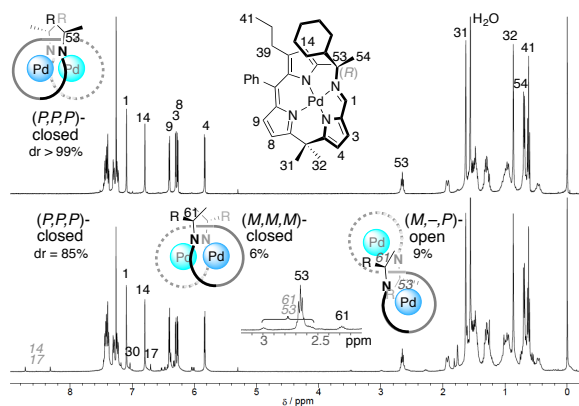


Fig. 6. ¹H NMR spectra of **4aPd** in CDCl₃ as an equilibrium mixture of (*P,P,P*)-closed form, (*M,M,M*)-closed form, and (*M,-,P*)-open form in 85:6:9 molar ratio (bottom) and as a single (*P,P,P*)-closed form (top). The 3,3'-protons (14 and 17) of the 2,2'-bipyrrrole subunit and the methine protons (53 and 61) at the stereogenic center are featured with black numbers for closed *C*₂ forms and with italic gray numbers for an open form (bottom). Signals due to the formimidoyl protons (1 and 30) are also marked (bottom).

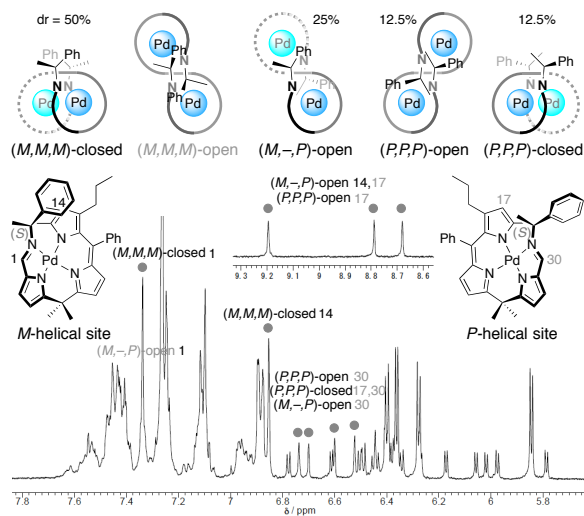


Fig. 7. ^1H NMR spectrum in the high frequency region of **3aPd** in CDCl_3 as an equilibrium mixture of four conformational isomers in 4:2:1:1. Nine singlets due to the 3,3'-protons (14 and 17) of the 2,2'-bipyrrrole subunit and the formimidoyl protons (1 and 30) are marked, but one formimidoyl proton (1) of a (*M*,*-*,*P*)-open form was not detected. Black numbers for *M*-helical coordination site and gray numbers for *P*-helical coordination site.

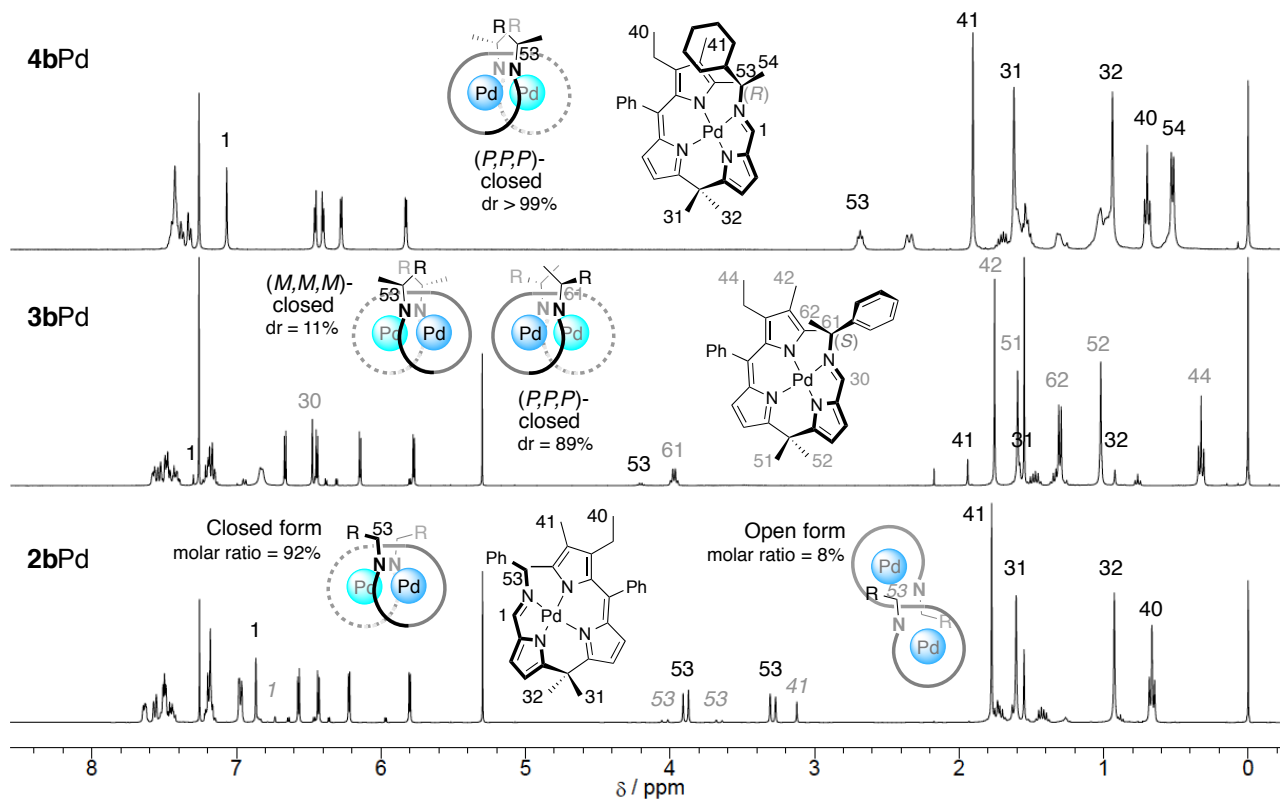


Fig. 8. ^1H NMR spectra of **2bPd** (bottom), **3bPd** (middle), and **4bPd** (top) in CDCl_3 . Selected signals are numbered according to the atom numbering scheme† of Fig. 2 and Scheme 4. Signals with gray italic numbers of **2bPd** are due to an open form (bottom). Signals with black numbers and gray numbers of **3bPd** are due to *M*- and *P*-helical coordination site, respectively (middle).

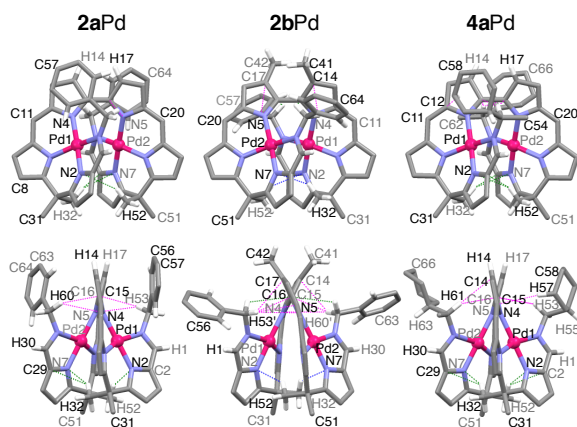


Fig. 9. X-ray diagrams of **2aPd** (left), **2bPd** (center), and **4aPd** (right) with an atom numbering scheme. Top and bottom rows show front and side views, respectively, with phenyl groups at C11 and C20 and alkyl groups at C13 and C18 omitted for clarity. Broken lines represent short contact. ¶#

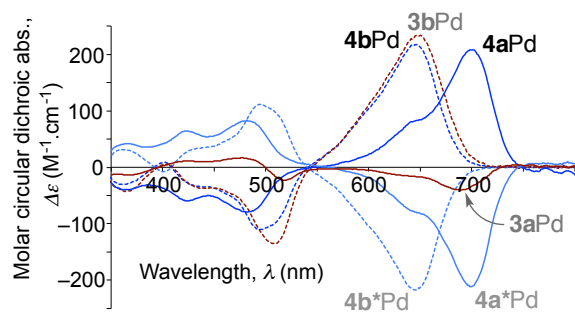


Fig. 10. CD spectra of bisPd complexes of hexapyrrole- α,ω -dicarbaldimines, **3aPd**, **4aPd**, **4a*Pd** (solid lines) and **3bPd**, **4bPd**, **4b*Pd** (broken lines), in CH_2Cl_2 .

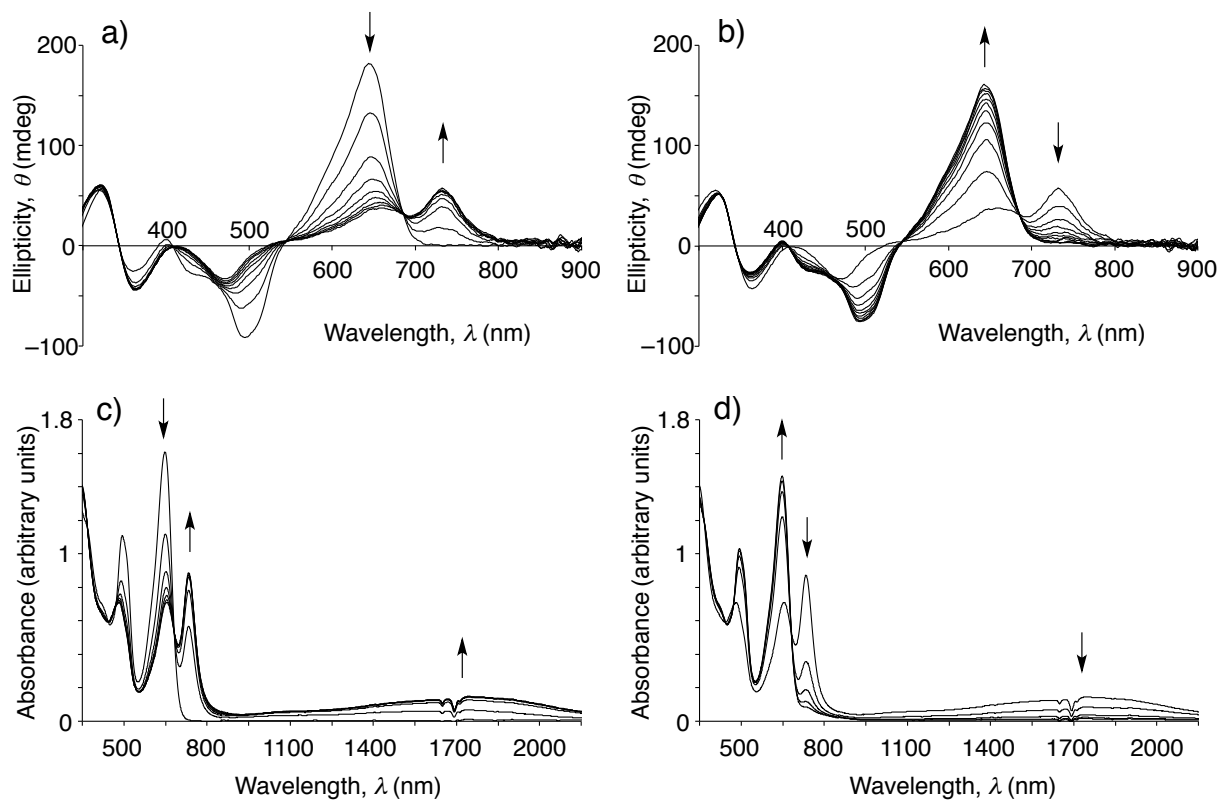
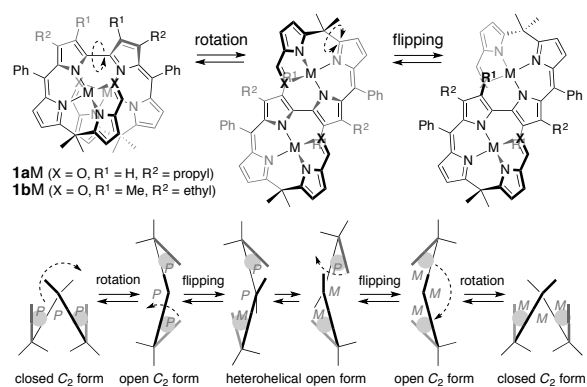
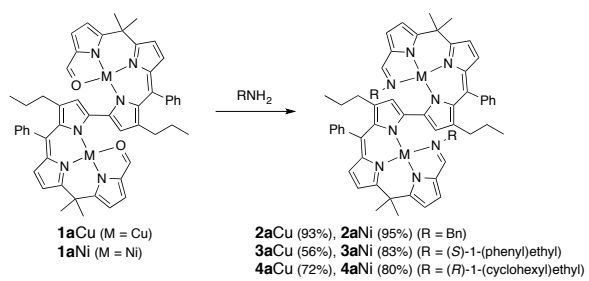


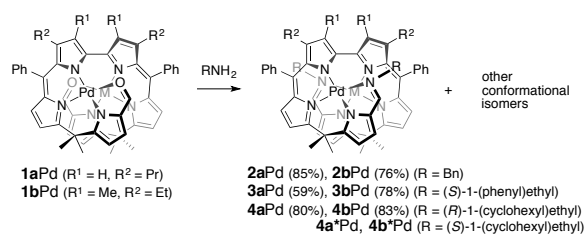
Fig. 11. CD spectral changes (top) upon electrolysis of **4bPd** in 0.1 M TBAP solution in CH_2Cl_2 with a Pt mesh electrode at (a) +0.50 V (vs. Ag/AgNO_3 reference electrode containing 0.1 M TBAP in MeCN) for 734 s followed by the potential at (b) +0.25 V for 1210 s. The Vis-NIR absorption spectral changes (bottom) upon electrolysis of **4bPd** at (c) +0.45 V for 1150 s followed by the potential at (d) +0.25 V for 766 s.



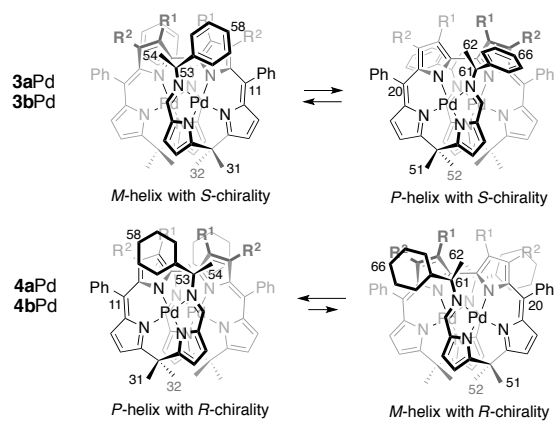
Scheme 1. Conformational changes of bimetallic complexes of hexapyrrole- α,ω -dicarbaldehyde ($X = O$) and dicarbaldimine ($X = NR$) (top) and their stick models as viewed along the bipyrrole $C(\text{pyrrole-}\alpha)-C(\text{pyrrole-}\alpha)$ bond (bottom). Curved arrows indicate rotation and flipping motions.



Scheme 2. Synthesis of bisCu and bisNi complexes of hexapyrrole- α,ω -dicarbaldimines.



Scheme 3. Synthesis of bisPd complexes of hexapyrrole- α,ω -dicarbaldimines.



Scheme 4. The equilibrium between *M*- and *P*-helical closed forms of **3aPd** and **3bPd** (top) and of **4aPd** and **4bPd** (bottom).

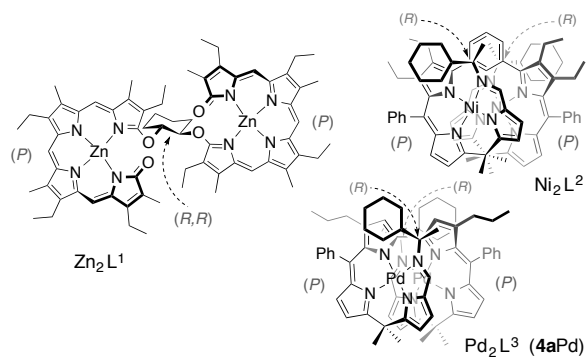


Chart 1. Long chain oligopyrrole helicates of high helical sense bias.

Table 1. Plane-to-plane angles and distances in the X-ray crystallography of the bimetallic complexes of hexapyrrole- α,ω -dicarbaldimines and dicarbaldehyde

	1aCu^a	4aNi	2aPd^b	2bPd	4aPd^b
< plane-to-plane angle (°) of adjacent two pyrrole rings >					
dipyrrolyl-methane	46.5 40.5	43.3 46.7	50.0 39.6	49.5 48.3	46.5 42.4
dipyrroline	19.2 24.7	16.4 21.7	10.4 9.6	18.4 22.2	11.8 11.7
2,2'-bi-pyrrole	157.9	175.3	22.6	50.3	26.3
< distance (Å) >					
M–N _{imine} ^c	2.089 ^d	1.964	2.101	2.091	2.094
M–N _{pyrrole} ^e	1.910	1.908	1.989	2.007	1.999
M–M	6.030	6.171	3.424	3.6293	3.4704

^a taken from our work [83]. ^b reported in our previous communication paper [91]. ^c averaged for two imine nitrogens. ^d Cu–O_{aldehyde} distance. ^e averaged for six pyrrole nitrogens.

Table 2. Cyclic voltammetric data of the bimetallic complexes^a

Complex	$E_{1/2}^b$	Complex	$E_{1/2}^b$	Complex	$E_{1/2}^b$
1aNi	+0.15	1aPd	+0.21	1bPd	+0.30
2aNi	+0.10	2aPd	+0.13	2bPd	+0.21
3aNi	+0.15	3aPd	+0.16	3bPd	+0.22
4aNi	+0.12	4aPd	+0.14	4bPd	+0.17

^a WE: glassy carbon, RE: Ag/AgNO₃ with 0.1 M tetrabutyl ammonium perchlorate (TBAP) in MeCN, CE: platinum wire, electrolyte: 0.1 M TBAP in CH₂Cl₂. ^b The mid-point potential ($E_{1/2}$ in V) for the first redox couple (M_2L/M_2L^+) referenced against a Fc/Fc⁺ couple.

Stereochemistry and chiroptical properties of bimetallic single helicates of hexapyrrole- α,ω -dicarbaldimines with high diastereoselectivity

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Stereogenic centers introduced at the terminal N-alkylcarbaldimines of the bimetallic oligopyrrole helicates induced high helical sense bias and their chiroptical properties in the Vis-NIR region were redox-tunable.

