Chiral Tectonics toward Square Planar Tetranuclear Pd(II) Complexes: Propagation of Axial Chirality through a Long Molecular Axis

Journal:	*Dalton Transactions*
Manuscript ID	DT-ART-05-2019-001913.R2
Article Type:	Paper
Date Submitted by the Author:	29-May-2019
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ARTICLE

Chiral Tectonics toward Square Planar Tetranuclear Pd(II) Complexes: Propagation of Axial Chirality through a Long Molecular Axis

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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An approach of molecular tectonics was applied to synthesize a tetranuclear Pd(II) complex with axial chirality, $[\{(L_t)Pd(II)(taet)Pd(II)\}_2(tpret)]$ (L_tH = benzoylacetone (bzacH) or 2-naphthoylacetone (npacH), taetH_2 = 1,1,2,2-tetraacetylethane and tpretH_2 = 1,1,2,2-tetrapropanoylethane). As a first step, a two-handed tecton, $[\{taetH\}Pd(II)]_2(tpret)]$, was synthesized. Next monomeric Pd(II) units were connected to both ends of the tecton to form a reactive tetranuclear intermediate, $[\{(hfac)Pd\ (II)(taet)Pd(II)\}_2(tpret)]$ (hfacH = hexafluoroacetylacetone). Finally terminal hfac's were replaced with the β-diketonato ligands having one or two bulky groups such as dibenzoylmethane (dbmH), bzacH and npacH. In case of the symmetrically substituted ligand (dbm), the formed complex was achiral and its structure was determined by single crystal X-ray analysis. In case of unsymmetical ligands (bzac and npac), the complexes were axially chiral due to the vertical twisting of the terminal ligands. The complexes were optically resolved chromatographycally on a chiral column. Their chiro-optical properties were investigated by means of electronic (ECD) and vibrational circular dichroism (VCD) spectroscopies. Notably the twisting relation between the two terminal ligands of the tetranuclear complexes influenced significantly chiral electronic properties, although they were separated by a distance longer than 3 nm.

Introduction

Stepwise assembly of metal coordination is an attractive approach with growing popularity for the functionalization of metal complexes.[1-4] One rational approach for this purpose is the technique of molecular tectonics, in which coordinating complexes are connected under the control of the number and direction of bridging ligands. The formed multi-nuclear complexes act as a supramolecular assembly in various functions such as multi-step catalytic activity, multi-electron redox reactions, gas adsorption and chiral recognition.[5-11]

In these attempts, a β-diketonato motif can be used as a versatile chelating group applicable to a wide scope of metal ions. As an isolated complex, tris(β-diketonato)metal(III) complexes have played an important role through their unique electronic and stereochemical properties.[4] One way to use the motif to the tectonics approach is to connect two β-diketonato moieties at the α-position to produce a bis-β-diketonato ligand.[12] A number of homo- and hetero-metallic multinuclear complexes have been prepared by use of this type of ligand as a bridging part. For example, Yu et al. have reported the bridging moieties containing O/N atoms to form the homo- and heterometallic complexes.[7]

We have developed a way to prepare multi-nuclear metal complexes by use of bis-β-diketonato ligands. What was noticed was that the β-diketonato moieties were vertically twisted, leading to the possibility of generating axial chirality. Motivated by this expectation, a number of chiral assemblies of metal complex units were produced by used of one- or two- or three-handed coordinating units as tectons. The method has been applied to bridge a wide scope of metal ions such as Al(III), Fe(III), Ni(II) and Pd(II).[13-16] It is now proposed that the method is denoted as "chiral tectonics".

Chiral tectonics was recently applied to the preparation of the dinuclear complexes bridging square-planar Pd(II) units.[17] Some of the compounds were used as a chiral dopant to induce chiral nematic phases in liquid crystals.[18] In the present work, the method was extended to synthesize tetranuclear Pd(II) complexes. A main attention was focussed on how the elongation of a molecular axis would affect the chiro-optical properties of a complex with axial chirality. Tetranuclear Pd(II) complexes were synthesized with a bis-β-diketonato (L_b or L_b') as a bridge and a substituted β-diketonato (L_t) at the terminal position (denoted by $[\{(L_t)Pd(II)(L_b)Pd(II)\}_2(L_b')]$). Their electronic (ECD) and vibrational circular dichroisms (VCD) spectra were recorded. The present results might be a benchmark to develop a polymeric square planar Pd(II) complex with axial chirality. Such a compound is regarded as an analogue of organic linear polymers with axial chirality.[19]

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^{1}H NMR,^{13}C NMR and mass analyses of Pd(II) complexes; The chromatographic resolution of tetranuclear Pd(II) complexes; The ECD spectra of dinuclear Pd(II) complexes; The calculated VCD spectra of dinuclear Pd(II) complexes; The crystal data and the table of selected bond lengths and torsion angles.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Results and Discussion

Preparation of tetranuclear Pd(II) complexes: A tetranucelar Pd(II) complex bridged by three bis-β-diketonato ligands in a straight fashion was prepared according to Chart 1. Firstly a dinuclear complex, [{(hfac)Pd(II)}$_2$(tpret)] (**1**, hfac = hexafluoroacetylacetonato, tpret = tetrapropanonylethanato) was obtained by reacting [(hfac)Pd(II)(μ-OMe)]$_2$ (**3**) with tetrapropanoylethane. **1** was converted to a two-handed tecton, [(taetH)Pd(II)]$_2$(tpret)] (**2**) by the action of an excess of tetraacetylethane on **1** in the presence of triethylamine. Connection of **2** with two Pd(II) units at the both sides using **3** gave [{(hfac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**4**). Thereafter **4** was treated with a 1,3-diketone in the presence of triethylamine to afford the final tetranuclear Pd(II) complex (**5**). Three kinds of 1,3-diketones were used in the last step and the corresponding symmetric complex [{(dbm)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5a**) and unsymmetric complexes, [{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5b**) and [{(npac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5c**) were obtained. These complexes **5** were identified by the ^{1}HNMR, ^{13}CNMR and mass spectra (ESI†).

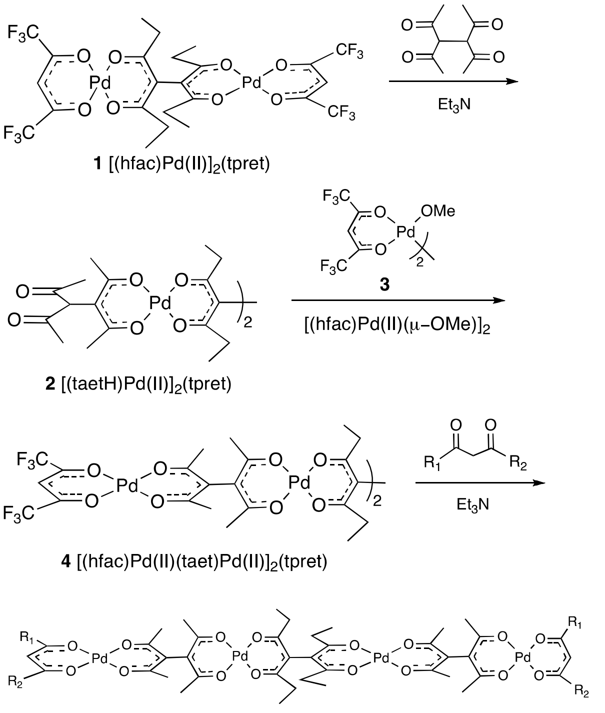

Chart 1. Synthesis of tetranuclear Pd(II) complexes: **5a** (R$_1$=Ph, R$_2$=Ph) [{(dbm)Pd(II)(taet)Pd(II)}$_2$(tpret)], **5b** (R$_1$=Ph, R$_2$=CH$_3$) [{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)], **5c** (R$_1$=Naph, R$_2$=CH$_3$) [{(npac)Pd(II)(taet)Pd(II)}$_2$(tpret)] .

The dinuclear Pd(II) complexes ([{(hfac)Pd(II)}$_2$(L$_b$)] and [{(L$_t$)Pd(II)}$_2$(taet)]) are shown in Chart 2 and 3.

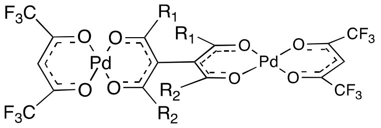

Chart 2. Dinuclear Pd(II) complex: **6** (R$_1$=Ph, R$_2$=CH$_3$) [{(hfac)Pd(II)}$_2$(dabe)].

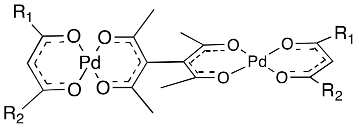

Chart 3. Dinuclear Pd(II) complexes: **7a** (R$_1$=Ph, R$_2$=CH$_3$) [{(bzac)Pd(II)}$_2$(taet)], **7b** (R$_1$=2-Naph, R$_2$=CH$_3$) [{(npac)Pd(II)}$_2$(taet)].

Single crystal X-Ray structural analyses: Among the obtained tetranuclear Pd(II) complexes, a single crystal was successfully obtained solely for the case of [{(dbm)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5a**). Figure 1 shows the achiral structure of the complex as determined by the X-ray crystallographic analysis. The four planar Pd(II) moieties were confirmed to be connected in a straight way by either taet or tpret ligands. The distance between the two terminal Pd(II) atoms was 2.396 nm. Accordingly the two terminal ligands groups were separated by ca. 3 nm. The bridging ligands (tpret or taet) were twisted nearly vertically.

The X-ray crystallographic analysis was achieved for a racemic dinuclear complex, [{(npac)Pd(II)}$_2$(taet)] (**7b**). Figure 2 shows the results of the analyses. The two planar Pd(II) moieties were vertically connected by the taet ligand. Since npac was unsymmetrically substituted, their twisting at the terminal positions caused axial chirality.

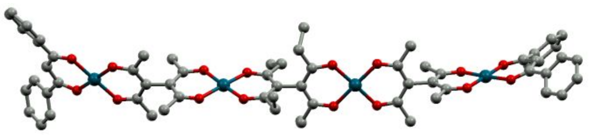

Figure 1. The X-ray drawing of achiral [{(dbm)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5a**). The four planar Pd(II) moieties were confirmed to be connected in a straight way by bridging ligands (taet or tpret) and symmetrical terminal ligand (dbm). Hydrogen atoms and solvent molecules are omitted for clarity.

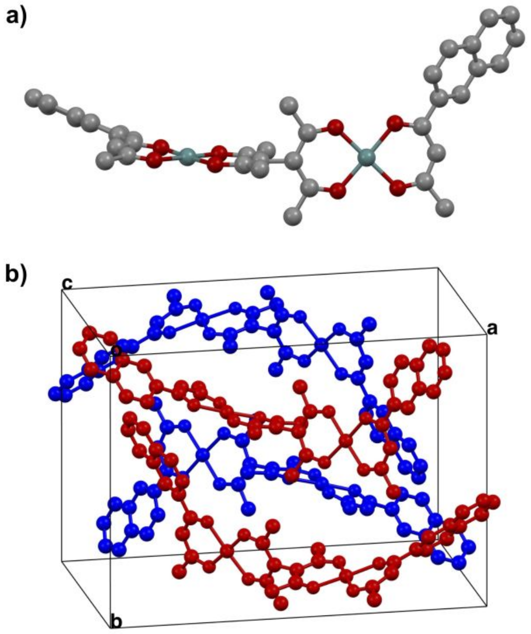

Figure 2. a) The X-ray drawing of [{(npac)Pd(II)}$_2$(taet)] (**7b**). b) Packing structures of [{(npac)Pd(II)}$_2$(taet)] (**7b**). *R* and *S* isomers are colored in red and blue, respectively. Hydrogen atoms and solvent molecules are omitted for clarity.

Electronic spectra of tetranuclear Pd(II) complexes: Figure 3 shows the UV-vis spectra of the dichloromethane solutions of the obtained tetranuclear and dinuclear complexes; [{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5b**) (grey solid line), [{(npac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5c**) (black solid broken line), [{(bzac)Pd(II)}$_2$(taet)] (**7a**) (grey broken line) and [{(npac)Pd(II)}$_2$(taet)] (**7b**) (black broken line).

According to the previous theoretical calculation for the dinuclear Pd(II) complexes, the peak at 250 nm was assigned as the combination of LMCT and π–π* transitions in the β-diketonato parts, while the peak at 350 nm was assinged mainly as the MLCT band.[17] The peak clearly observed at 220 nm was ascribed to the "npac" terminal ligands. The molar adsorption coefficients of the tetranuclear complexes were nearly doubled in comparison to those of the component dinuclear complexes over the whole wavelength range. It suggested that each Pd(II) unit was electronically independent in these polymeric species.

Optical resolution and measurements of electronic circular dichroism (ECD) spectra: Optical resolution was attempted by high performance liquid chromatography (HPLC) using a chiral column (Experimental section). When racemic tetranuclear complexes (**5b**) and (**5c**) were eluted on the column, two peaks with an equal area were obtained (ESI†).

The electronic circular dichroism (ECD) spectra of the less and more retaining fractions were recorded in dichloromethane solutions. They gave mirror-imaged spectra in the range of 240 - 450 nm as shown in Figure 4. The results confirmed the achievement of optical resolution.

The peaks in the range of 240 - 300 nm of the ECD spectra corresponded to the π–π* absorption in the same wavelength range of the electronic absorption spectra. The band split to two composites, the one a small peak at 260 nm and the other a large peak at 250 nm. It was noted that these peaks showed the same signs in case of [{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5b**), while they showed the opposite sign in the case of [{(npac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5c**). The behaviours were unexpected from the exciton coupling between the two twisting parts of ligands, since it always predicted the opposite signs of the split peaks. Probably the structural difference of bridging β-diketonato ligands caused additional effects on the signs of the splitted peaks between the two complexes. There was a broad band around 350 nm. This corresponded to the MLCT band in the electronic absorption spectra. The two complexes gave the same signs for this band.

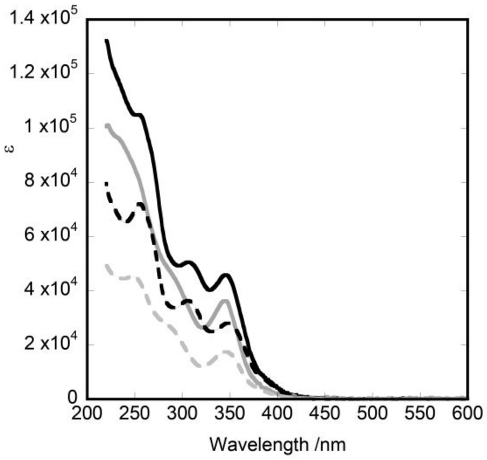

Figure 3. The electronic absorption spectra of [{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5b**) (grey solid line) [{(npac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5c**) (black solid line) [{(bzac)Pd(II)}$_2$(taet)] (**7a**) (grey broken line) and [{(npac)Pd(II)}$_2$(taet)] (**7b**) (black broken line) The solvent was dichloromethane.

The ECD spectra of the tetranuclear complexes, [{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5b**) and [{(npac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5c**), were compared with those of the dinuclear complexes, [{(bzac)Pd(II)}$_2$(taet)] (**7a**) and [{(npac)Pd(II)}$_2$(taet)] (**7b**), respectively. The ECD spectra of the dinuclear complexes in acetonitrile are shown in the supporting information(ESI†). These ECD spectra were very similar between the tetranuclear and dinuclear complexes over the whole wavelength region.

The absolute configuration of the dinuclear complexes was determined from the VCD spectra as will be described in the following section. According to it, the enantiomer giving the negative or positive band in the MLCT band around 350 nm were assigned to be *R*- or *S*-enantiomers, respectively. Based on this, the less and more retaining fractions contained *R*- and *S*-isomers, respectively.

The axial chirality in the present complexes was caused by the vertically twisting of two unsymmetrically substituted terminal ligands. On the basis of the molecular structures (Figures 1 and 2), the distance between the two terminal ligands was estimated to be 1.5 nm and 3.0 nm for the dinuclear and tetranuclear complexes, respectively. It was interesting to note how the elongation of the distance affects the chiro-optical properties of the complexes. As a result, the intensity of the ECD bands at 240 nm for a tetranuclear complex, [{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5b**), was half of those of the corresponding bands for a dinuclear complex, [{(bzac)Pd(II)}$_2$(taet)] **(7a)**. As for the [{(npac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5c**), the intensity of the corresponding band was one-third of that of [{(npac)Pd(II)}$_2$(taet)] (**7b**). The results indicated that the electronic effects caused by the twisting of the two terminal benzyl or naphthyl groups well propagated through the molecular axis with little decay, even when they were separated by 3 nm in case of the tetranuclear complexes.

VCD measurements of dinulcear and tetranuclear Pd(II) complexes: The VCD was recorded on the dinuclear and tetranuclear Pd(II) complexes with a purpose of studying the elongation effects of a molecular axis on their vibrational chiral properties. The spectroscopy has been applied previously for various types of chiral metal complexes.[20-28] As far as our literature survey is concerned, there are few applications of multi-nuclear metal complexes with no asymmetric carbon.

Figure 5 shows the experimental IR and VCD spectra of [{(hfac)Pd(II)}$_2$(dabe)] (dabe =1,2-diacetyl-1,2-dibenzoylethanato) (**6**), [{(bzac)Pd(II)}$_2$(taet)] (**7a**) and [{(npac)Pd(II)}$_2$(taet)] (**7b**). The former compound was axially chiral due to the twisting of two phenyl groups in the bridging ligand (dabe^{2-}).[17] The two phenyl groups were separated by 0.35 nm. In contrast, the latter compounds were axially chiral due to the substituted moieties at the terminal positions. They were separated by 1.5 nm. For all these dimers, the VCD signals showed the mirror-image relation between the antipodal pairs, confirming the reliability of the spectra. The experimental IR and VCD spectra were compared with the DFT calculation on the basis. The calculated IR and VCD were shown in the supporting information. As shown by numbering the corresponded peaks, the calculated spectrum well reproduced the observed one. The assignment of VCD peaks is summarized in Table S1(a)-(c) (supporting information). In [{(hfac)Pd(II)}$_2$(dabe)] (**6**), the stretching vibration of bridging dabe ligands are observed at the mirror-image in 1300-1450 cm^{-1}. On the other hand, in case of [{(bzac)Pd(II)}$_2$(taet)] (**7a**) and [{(npac)Pd(II)}$_2$(taet)] (**7b**), only terminal unsymmetrical C-C-C stretching was clearly observed around 1500 cm^{-1}.

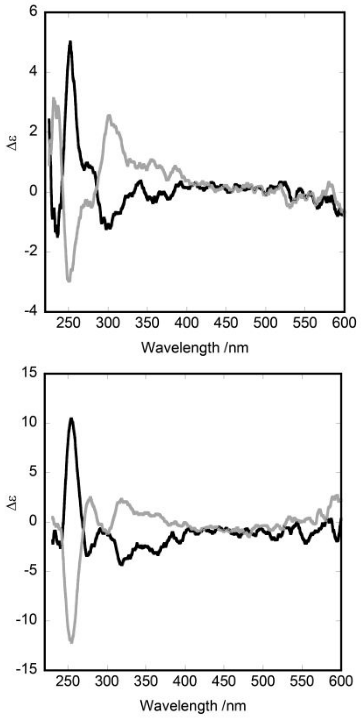

Figure 4. The ECD spectra of [{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5b**) (upper) and [{(npac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5c**) (lower) resolved on a chiral column. The solid and grey lines indicated the less and more retaining fractions, respectively. The solvent was dichloromethane.

Notably the magnitude of $\Delta\varepsilon$ was of the same order among these three compounds (i.e. 0.05, 0.1 and 0.15 for the peak at the most intense peaks in case of [{(hfac)Pd(II)}$_2$(dabe)] (**6**), [{(bzac)Pd(II)}$_2$(taet)] (**7a**) and [{(npac)Pd(II)}$_2$(taet)] (**7b**), respectively). The results indicated that the chiral nature caused by the vertical twisting of substituted groups propagated along the molecular axis beyond two Pd(II) units. As for the absolute configuration, the less and more retaining fractions were concluded to contain *R*- and *S*-isomers in case of [{(bzac)Pd(II)}$_2$(taet)] (**7a**) and [{(npac)Pd(II)}$_2$(taet)] (**7b**), respectively.

The VCD measurements were performed for tetranuclear complexes, [{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5b**) and [{(npac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5c**). No VCD peaks were, however, detected under the similar experimental conditions. The results implied that the chiral nature of molecular vibrations was unable to go beyond three Pd(II) units.

The situations were in contrast with the appearance of ECD for the same complexes. In other words, the vibrational chirality decayed more rapidly than the electronic ones. Presently the improvement of the machine with higher sensitivity is now under progress.

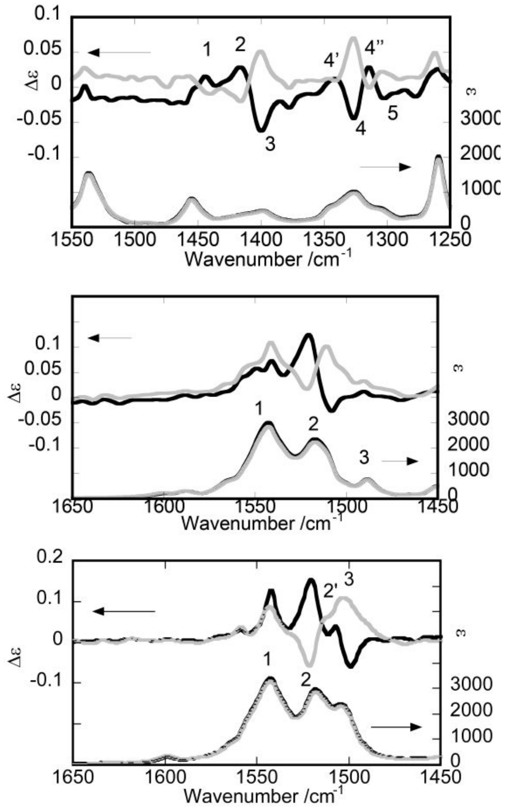

Figure 5. The experimental VCD spectra of the less retaining fraction (solid line) and the more retaining fraction (grey line) of [{(hfac)Pd(II)}$_2$(dabe)] (**6**) (upper) [{(bzac)Pd(II)}$_2$(taet)] (**7a**) (middle) and [{(npac)Pd(II)}$_2$(taet)] (**7b**) (lower) resolved on the chiral column. The solvent was $CDCl_3$. Correction was made to exclude the contribution of solvents from IR spectra.

Experimental

Syntheses of tetranuclear complexes

[{(hfac)Pd(II)}$_2$(tpret)] (1): The complex was synthesized according to the procedure reported previously.[17]

[{(taetH)Pd(II)}$_2$(tpret)] (2): To a dichloromethane (25 mL) solution of [{(hfac)Pd(II)}$_2$(tpret)] (211.0 mg, 0.24 mmol) and taetH$_2$ (237.5 mg, 1.32 mmol) was added dropwise triethylamine (182 µL, 1.32 mmol) at 0-5 °C, and the mixture was stirred at room temperature for 2.5 hours. After evaporation, the residue was treated with a limited amount of ethanol to give a yellow powder, which was purified by silica gel flash chromatography (chloroform) and HPLC on silica gel column (4 mm (i.d.) × 25 cm; GL Science, Japan, 2% methanol-dichloromethane) to afford [{(taetH)Pd(II)}$_2$(tpret)] in 17% yield.

[{(hfac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (4): A dichloromethane (3 mL) solution of [{(taetH)Pd(II)}$_2$(tpret)] (13.1 mg, 0.015 mmol) and [{(hfac)Pd(II)}$_2$(µ-OMe)] (13.7 mg, 0.020 mmol) was stirred for three days at room temperature. After removal of volatile materials, the residue was washed with hexane and dried in vacuo to give [{(hfac)Pd(II)(taet)Pd(II)}$_2$(tpret)]. The product was used without further purification.

[{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (5b): To a dichloromethane (2 mL) solution of [{(hfac)Pd(II) (taet)Pd(II)}$_2$(tpret)] obtained above and bzacH (7.3 mg, 0.045 mmol) was added dropwise triethylamine (9 µL, 0.06 mmol) and the mixture was stirred for 2.5 hours at room temperature. After evaporation, the residue was purified by silica gel flash chromatography (chloroform) and HPLC using silica gel column (0.8% methanol-dichloromethane) to give [{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)] in 73% yield.

[{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (5b). ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.83 (4H, broad d, *J*=7.5 Hz, *o*-H), 7.47 (2H, broad t, *J*=7.5 Hz, *p*-H), 7.38 (4H, t, *J*=7.5 Hz, *m*-H), 6.06 (2H, s, CH), 2.20 (6H, s, CH_3), 2.15 (8H, q, *J*=7.5 Hz, CH_2), 1.973 (6H, s, CH_3), 1.969 (6H, s, CH_3), 1.96 (12H, s, CH_3), 1.02 ppm (12H, t, *J*=7.5 Hz, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ=190.5 (twice in integral ratio to signals of other carbonyl carbon atoms, C_{CO}), 188.9 (C_{CO}), 188.0 (C_{CO}), 187.9 (twice, C_{CO}), 187.6 (C_{CO}), 180.5 (C_{CO}), 135.9 (C_{arom}), 131.5 (C_{arom}), 128.3 (*o*-C_{arom}), 127.5 (*m*-C_{arom}), 112.1 (twice, C_{vinyl}), 110.1 (C_{vinyl}), 98.6 (C_{vinyl}), 31.5 ($C_{methylene}$), 26.21 (twice, C_{methyl}), 26.17 (C_{methyl}), 26.09 (C_{methyl}), 26.01 (C_{methyl}), 9.9 ($C_{methyl\ in\ Et}$) ppm; HRMS (ESI$^+$, CH_3CN/H_2O) calcd for $C_{54}H_{62}O_{16}Pd_4+H^+$ 1391.0286, found *m/z*=1391.0299 [M+H$^+$].

Tetranuclear complexes [{(dbm)Pd(II)(taet)Pd(II)}$_2$(tpret)] **(5a)** and [{(npac)Pd(II)(taet)Pd(II)}$_2$(tpret)] **(5c)** were synthesized in a similar manner as above by the respective use of dbmH and npacH.

Dinuclear complexes [{(hfac)Pd(II)}$_2$(dabe)] (**6**) and [{(bzac)Pd(II)}$_2$(taet)] (**7a**) were reported in the previous paper.[17] Dinuclear complex [{(npac)Pd(II)}$_2$(taet)] **(7b)** was synthesized in a manner similar to preparation of **7a**.

[{(npac)Pd(II)}$_2$(taet)] (7b). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.38 (2H, s, aromatic H_1), 7.91-7.81 (8H, aromatic $H_{3,4,5,8}$), 7.53 (2H, broad t, *J*=8.0 Hz , aromatic H_6), 7.49 (2H, broad t, *J*=8.0 Hz , aromatic H_7), 6.23 (2H, s, CH), 2.26 (6H, s, CH_3), 2.03 (6H, s, CH_3), 2.01 ppm (6H, s, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ=188.9 (C_{CO}), 188.1 (C_{CO}), 187.7 (C_{CO}), 180.2 (C_{CO}), 134.8 (C_{arom}), 133.1 (C_{arom}), 132.6 (C_{arom}), 129.2 (C_{arom}), 128.3 (C_{arom}), 128.0 (C_{arom}), 127.7 (C_{arom}), 127.6 (C_{arom}), 126.5 (C_{arom}). 124.1 (C_{arom}), 112.2 (C_{vinyl}), 98.9 (C_{vinyl}), 26.2 (C_{methyl}), 26.1 (C_{methyl}), 26.0 (C_{methyl}) ppm; HRMS (FAB$^+$, 3-NBA) calcd for $C_{38}H_{34}O_8Pd_2+H^+$ 833.0406, found *m/z*=833.0433 [M+H].

Optical resolution of racemic tetranuclear and dinuclear complexes

Racemic tetranuclear complexes, [{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5b**) and [{(npac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5c**), were resolved respectively on a chiral column (4 mm (i.d.) × 25 cm; CHIRALPACK IC, Daicel, Japan) with dichloromethane containing 0.07% methanol. The ECD spectra of enantiomers thus resolved were recorded. Some of the chromatograms are given in ESI†. Racemic dinuclear complexes, [{(hfac)Pd(II)}$_2$(dabe)] (**6**), [{(bzac)Pd(II)}$_2$(taet)] (**7a**) and [{(npac)Pd(II)}$_2$(taet)] **(7b),** were all optically resolved in the same way as was reported in the previous paper.[17]

X-Ray chrystallographic analyses

X-Ray diffraction analysis was performed using a Rigaku VariMax with a Saturn diffractometer using multilayer mirror monochromated Mo Kα radiation (λ = 0.71073 Å) at 100 ± 1 K. The crystals were mounted in cryoloops. Collection of the reflection intensities and determination of the cell parameters were performed using CrystalClear (Rigaku)[29] and CrysAlisPro (Rigaku Oxford Diffraction).[30] Data were corrected for Lorentz polarization and absorption effects. The structures were solved using SHELXT 2018/2[31] and expanded using the Fourier technique. All calculations were performed using the CrystalStructure crystallographic software package[32] and SHELXL-2018/3[33] was used for structure refinement. Data were validated using PLATON.[34] Single crystals of [{(dbm)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5a**) were prepared by evaporating a $C_6H_5CH_3/C_2H_5OH$ solution. Crystallographic data: $C_{64}H_{66}O_{16}Pd_4 \cdot 2(C_7H_8)$, formula weight 1701.04, triclinic, P-1, a = 13.9277(3) Å, b = 14.8370(3) Å, c = 19.9949(4) Å, α = 104.707(2)˚, β = 100.001(2)˚, γ = 108.914(2)˚, V = 3629.76(16) Å^3, Z = 2, T = 100 K, λ = 0.71073 Å, μ = 1.042 mm^{-1}. R_1 = 0.0499 ($I > 2\sigma(I)$), wR_2 = 0.1026 (all data), GOF = 1.025 ($I > 2\sigma(I)$), CCDC No. 1910079. Single crystals of [{(npac)Pd(II)}$_2$(taet)] (**7b**) were obtained by recrystallization from 1,2-dichloroethane/n-hexane. Crystallographic data: $C_{38}H_{34}O_8Pd_2 \cdot C_2H_2Cl_4$, formula weight: 999.29, $P2_1/c$, a = 21.4114(6) Å, b = 16.1953(4) Å, c = 11.4025(2) Å, α = 90˚, β = 94.113(2)˚, γ = 90˚ V = 3943.79(16) Å^3, Z = 4, T = 100 K, λ = 0.71073 Å, μ = 1.235 mm^{-1}. R = 0.0420 ($I > 2\sigma(I)$), wR_2 = 0.0900 (all data), GOF = 1.023 ($I > 2\sigma(I)$), CCDC No.1910080.

Instrumentation: NMR spectra were obtained using a spectrometer, AVIII500 (Bruker). UV-visible electronic spectra were recorded with UV-vis spectrophotometer (U-2810, Hitachi Ltd., Japan). Circular dichroism spectra were measured with a polarimeter (J-720, Jasco, Japan).

Spectroscopic measurements: The VCD spectra were measured with a machine developed in our laboratory with corporation of JASCO Co. Ltd., Japan (PRESTO-S-2016 VCD/LD spectrometer).[27] The machine was a concurrent system in combination with linear dichroism. The machine is the single PEM system. The calibration was made by use of a quarter wave-retardation and an analyser. A $CDCl_3$ solution of the complex (ca.0.02 M) was injected into a cell (200 μm in optical length) with BaF_2 windows. The signal was accumulated during 10000 scans for each complex. The resolution of wavenumber was 4 cm^{-1}. The baseline correction was performed for the IR spectra by subtracting the solvent contribution.

Computational details

The VCD and IR of Pd(II) complexes were theoretically calculated by use of Gaussian 16 program or Gaussian 09 program.[35] Geometry optimization was performed at the DFT level (B3LYP functional with Stuttgart ECP for Pd(II) and 6-31G(d,p) for the other atoms) in the ground states. The VCD intensities were determined by the vibrational rotational strength and the magnetic dipole moments, which were calculated by the magnetic field perturbation (MFP) theory formulated using magnetic field gauge-invariant atomic orbitals. The calculated intensities were converted to Lorentzian bands with 4 cm^{-1} half-width at half-height. The observed spectra were assigned on the basis of animations of the molecular vibration with Gauss view 6.0 (Gaussian Inc.).

Conclusions

Tetranulcear and dinuclear square planar Pd(II) complexes were prepared by use of bis-β-diketonato ligands. These complexes were axially chiral due to the vertical twisting of the β-diketonato moieties. The present work provides a way to introduce axial chirality to achiral square planar moieties. The present strategy is simpler and can be a benchmark for developing the chiral tectonics of polymeric square planar Pd(II) complexes with axial chirality.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The acknowledgements come at the end of an article after the conclusions and before the notes and references.

This work was financially supported by the JSPS KAKENHI Grant-in-Aid for Scientific Research (B) JP17H03044 and JST MIRAI grants (JPMJMI18GC). The computations were performed using the Research Center for Computational Science, Okazaki, Japan.

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Chiral Tectonics toward Square Planar Tetranuclear Pd(II) Complexes: Propagation of Axial Chirality through a Long Molecular Axis

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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An approach of molecular tectonics was applied to synthesize a tetranuclear Pd(II) complex with axial chirality, $[\{(L_t)Pd(II)(taet)Pd(II)\}_2(tpret)]$ (L_tH = benzoylacetone (bzacH) or 2-naphthoylacetone (npacH), taetH_2 = 1,1,2,2-tetraacetylethane and tpretH_2 = 1,1,2,2-tetrapropanoylethane). As a first step, a two-handed tecton, $[\{taetH\}Pd(II)]_2(tpret)]$, was synthesized. Next monomeric Pd(II) units were connected to both ends of the tecton to form a reactive tetranuclear intermediate, $[\{(hfac)Pd\ (II)(taet)Pd(II)\}_2(tpret)]$ (hfacH = hexafluoroacetylacetone). Finally terminal hfac's were replaced with the β-diketonato ligands having one or two bulky groups such as dibenzoylmethane (dbmH), bzacH and npacH. In case of the symmetrically substituted ligand (dbm), the formed complex was achiral and its structure was determined by single crystal X-ray analysis. In case of unsymmetical ligands (bzac and npac), the complexes were axially chiral due to the vertical twisting of the terminal ligands. The complexes were optically resolved chromatographycally on a chiral column. Their chiro-optical properties were investigated by means of electronic (ECD) and vibrational circular dichroism (VCD) spectroscopies. Notably the twisting relation between the two terminal ligands of the tetranuclear complexes influenced significantly chiral electronic properties, although they were separated by a distance longer than 3 nm.

Introduction

Stepwise assembly of metal coordination is an attractive approach with growing popularity for the functionalization of metal complexes.[1-4] One rational approach for this purpose is the technique of molecular tectonics, in which coordinating complexes are connected under the control of the number and direction of bridging ligands. The formed multi-nuclear complexes act as a supramolecular assembly in various functions such as multi-step catalytic activity, multi-electron redox reactions, gas adsorption and chiral recognition.[5-11]

In these attempts, a β-diketonato motif can be used as a versatile chelating group applicable to a wide scope of metal ions. As an isolated complex, tris(β-diketonato)metal(III) complexes have played an important role through their unique electronic and stereochemical properties.[4] One way to use the motif to the tectonics approach is to connect two β-diketonato moieties at the α-position to produce a bis-β-diketonato ligand.[12] A number of homo- and hetero-metallic multinuclear complexes have been prepared by use of this type of ligand as a bridging part. For example, Yu et al. have reported the bridging moieties containing O/N atoms to form the homo- and heterometallic complexes.[7]

We have developed a way to prepare multi-nuclear metal complexes by use of bis-β-diketonato ligands. What was noticed was that the β-diketonato moieties were vertically twisted, leading to the possibility of generating axial chirality. Motivated by this expectation, a number of chiral assemblies of metal complex units were produced by used of one- or two- or three-handed coordinating units as tectons. The method has been applied to bridge a wide scope of metal ions such as Al(III), Fe(III), Ni(II) and Pd(II).[13-16] It is now proposed that the method is denoted as “chiral tectonics”.

Chiral tectonics was recently applied to the preparation of the dinuclear complexes bridging square-planar Pd(II) units.[17] Some of the compounds were used as a chiral dopant to induce chiral nematic phases in liquid crystals.[18] In the present work, the method was extended to synthesize tetranuclear Pd(II) complexes. A main attention was focussed on how the elongation of a molecular axis would affect the chiro-optical properties of a complex with axial chirality. Tetranuclear Pd(II) complexes were synthesized with a bis-β-diketonato (L_b or L_b’) as a bridge and a substituted β-diketonato (L_t) at the terminal position (denoted by $[\{(L_t)Pd(II)(L_b)Pd(II)\}_2(L_b')]$). Their electronic (ECD) and vibrational circular dichroisms (VCD) spectra were recorded. The present results might be a benchmark to develop a polymeric square planar Pd(II) complex with axial chirality. Such a compound is regarded as an analogue of organic linear polymers with axial chirality.[19]

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^{1}H NMR,^{13}C NMR and mass analyses of Pd(II) complexes; The chromatographic resolution of tetranuclear Pd(II) complexes; The ECD spectra of dinuclear Pd(II) complexes; The calculated VCD spectra of dinuclear Pd(II) complexes; The crystal data and the table of selected bond lengths and torsion angles.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Results and Discussion

Preparation of tetranuclear Pd(II) complexes: A tetranucelar Pd(II) complex bridged by three bis-β-diketonato ligands in a straight fashion was prepared according to Chart 1. Firstly a dinuclear complex, [{(hfac)Pd(II)}$_2$(tpret)] (**1**, hfac = hexafluoroacetylacetonato, tpret = tetrapropanonylethanato) was obtained by reacting [(hfac)Pd(II)(μ-OMe)]$_2$ (**3**) with tetrapropanoylethane. **1** was converted to a two-handed tecton, [(taetH)Pd(II)]$_2$(tpret)] (**2**) by the action of an excess of tetraacetylethane on **1** in the presence of triethylamine. Connection of **2** with two Pd(II) units at the both sides using **3** gave [{(hfac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**4**). Thereafter **4** was treated with a 1,3-diketone in the presence of triethylamine to afford the final tetranuclear Pd(II) complex (**5**). Three kinds of 1,3-diketones were used in the last step and the corresponding symmetric complex [{(dbm)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5a**) and unsymmetric complexes, [{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5b**) and [{(npac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5c**) were obtained. These complexes **5** were identified by the ^{1}HNMR, ^{13}CNMR and mass spectra (ESI†).

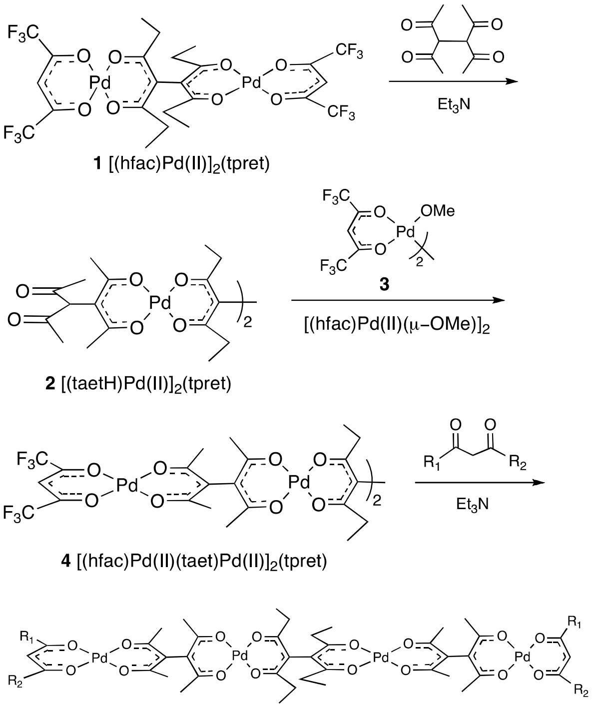

Chart 1. Synthesis of tetranuclear Pd(II) complexes: **5a** (R$_1$=Ph, R$_2$=Ph) [{(dbm)Pd(II)(taet)Pd(II)}$_2$(tpret)], **5b** (R$_1$=Ph, R$_2$=CH$_3$) [{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)], **5c** (R$_1$=Naph, R$_2$=CH$_3$) [{(npac)Pd(II)(taet)Pd(II)}$_2$(tpret)] .

The dinuclear Pd(II) complexes ([{(hfac)Pd(II)}$_2$(L$_b$)] and [{(L$_t$)Pd(II)}$_2$(taet)]) are shown in Chart 2 and 3.

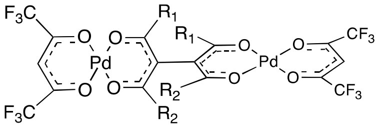

Chart 2. Dinuclear Pd(II) complex: **6** (R$_1$=Ph, R$_2$=CH$_3$) [{(hfac)Pd(II)}$_2$(dabe)].

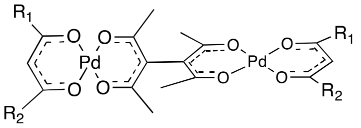

Chart 3. Dinuclear Pd(II) complexes: **7a** (R$_1$=Ph, R$_2$=CH$_3$) [{(bzac)Pd(II)}$_2$(taet)], **7b** (R$_1$=2-Naph, R$_2$=CH$_3$) [{(npac)Pd(II)}$_2$(taet)].

Single crystal X-Ray structural analyses: Among the obtained tetranuclear Pd(II) complexes, a single crystal was successfully obtained solely for the case of [{(dbm)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5a**). Figure 1 shows the achiral structure of the complex as determined by the X-ray crystallographic analysis. The four planar Pd(II) moieties were confirmed to be connected in a straight way by either taet or tpret ligands. The distance between the two terminal Pd(II) atoms was 2.396 nm. Accordingly the two terminal ligands groups were separated by ca. 3 nm. The bridging ligands (tpret or taet) were twisted nearly vertically.

The X-ray crystallographic analysis was achieved for a racemic dinuclear complex, [{(npac)Pd(II)}$_2$(taet)] (**7b**). Figure 2 shows the results of the analyses. The two planar Pd(II) moieties were vertically connected by the taet ligand. Since npac was unsymmetrically substituted, their twisting at the terminal positions caused axial chirality.

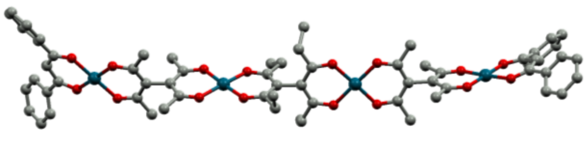

Figure 1. The X-ray drawing of achiral [{(dbm)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5a**). The four planar Pd(II) moieties were confirmed to be connected in a straight way by bridging ligands (taet or tpret) and symmetrical terminal ligand (dbm). Hydrogen atoms and solvent molecules are omitted for clarity.

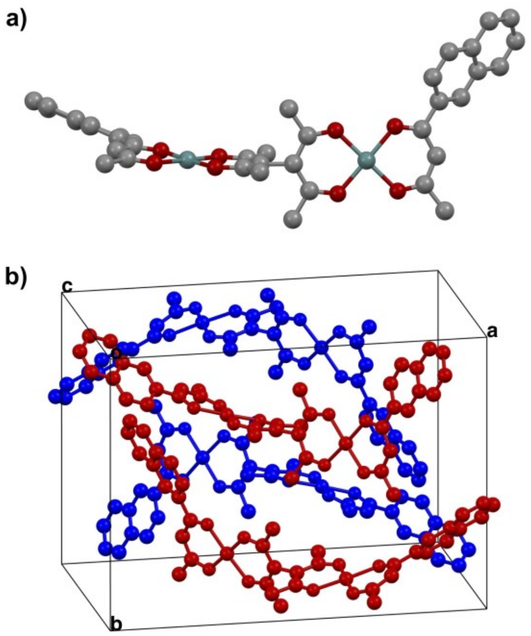

Figure 2. a) The X-ray drawing of [{(npac)Pd(II)}$_2$(taet)] (**7b**). b) Packing structures of [{(npac)Pd(II)}$_2$(taet)] (**7b**). *R* and *S* isomers are colored in red and blue, respectively. Hydrogen atoms and solvent molecules are omitted for clarity.

Electronic spectra of tetranuclear Pd(II) complexes: Figure 3 shows the UV-vis spectra of the dichloromethane solutions of the obtained tetranuclear and dinuclear complexes; [{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5b**) (grey solid line), [{(npac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5c**) (black solid broken line), [{(bzac)Pd(II)}$_2$(taet)] (**7a**) (grey broken line) and [{(npac)Pd(II)}$_2$(taet)] (**7b**) (black broken line).

According to the previous theoretical calculation for the dinuclear Pd(II) complexes, the peak at 250 nm was assigned as the combination of LMCT and $\pi-\pi^*$ transitions in the β-diketonato parts, while the peak at 350 nm was assinged mainly as the MLCT band.[17] The peak clearly observed at 220 nm was ascribed to the "npac" terminal ligands. The molar adsorption coefficients of the tetranuclear complexes were nearly doubled in comparison to those of the component dinuclear complexes over the whole wavelength range. It suggested that each Pd(II) unit was electronically independent in these polymeric species.

Optical resolution and measurements of electronic circular dichroism (ECD) spectra: Optical resolution was attempted by high performance liquid chromatography (HPLC) using a chiral column (Experimental section). When racemic tetranuclear complexes (**5b**) and (**5c**) were eluted on the column, two peaks with an equal area were obtained (ESI†).

The electronic circular dichroism (ECD) spectra of the less and more retaining fractions were recorded in dichloromethane solutions. They gave mirror-imaged spectra in the range of 240 - 450 nm as shown in Figure 4. The results confirmed the achievement of optical resolution.

The peaks in the range of 240 - 300 nm of the ECD spectra corresponded to the $\pi-\pi^*$ absorption in the same wavelength range of the electronic absorption spectra. The band split to two composites, the one a small peak at 260 nm and the other a large peak at 250 nm. It was noted that these peaks showed the same signs in case of [{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5b**), while they showed the opposite sign in the case of [{(npac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5c**). The behaviours were unexpected from the exciton coupling between the two twisting parts of ligands, since it always predicted the opposite signs of the split peaks. Probably the structural difference of bridging β-diketonato ligands caused additional effects on the signs of the splitted peaks between the two complexes. There was a broad band around 350 nm. This corresponded to the MLCT band in the electronic absorption spectra. The two complexes gave the same signs for this band.

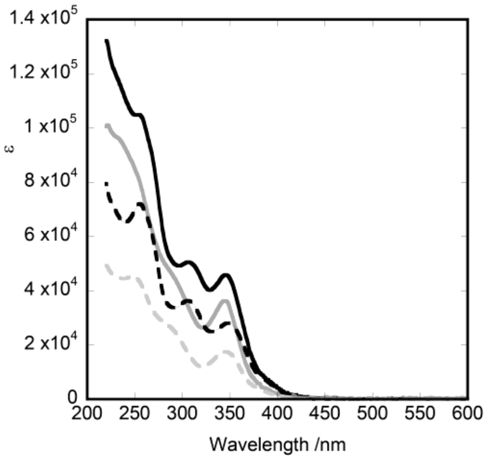

Figure 3. The electronic absorption spectra of [{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5b**) (grey solid line) [{(npac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5c**) (black solid line) [{(bzac)Pd(II)}$_2$(taet)] (**7a**) (grey broken line) and [{(npac)Pd(II)}$_2$(taet)] (**7b**) (black broken line) The solvent was dichloromethane.

The ECD spectra of the tetranuclear complexes, [{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5b**) and [{(npac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5c**), were compared with those of the dinuclear complexes, [{(bzac)Pd(II)}$_2$(taet)] (**7a**) and [{(npac)Pd(II)}$_2$(taet)] (**7b**), respectively. The ECD spectra of the dinuclear complexes in acetonitrile are shown in the supporting information(ESI†). These ECD spectra were very similar between the tetranuclear and dinuclear complexes over the whole wavelength region.

The absolute configuration of the dinuclear complexes was determined from the VCD spectra as will be described in the following section. According to it, the enantiomer giving the negative or positive band in the MLCT band around 350 nm were assigned to be *R*- or *S*-enantiomers, respectively. Based on this, the less and more retaining fractions contained *R*- and *S*-isomers, respectively.

The axial chirality in the present complexes was caused by the vertically twisting of two unsymmetrically substituted terminal ligands. On the basis of the molecular structures (Figures 1 and 2), the distance between the two terminal ligands was estimated to be 1.5 nm and 3.0 nm for the dinuclear and tetranuclear complexes, respectively. It was interesting to note how the elongation of the distance affects the chiro-optical properties of the complexes. As a result, the intensity of the ECD bands at 240 nm for a tetranuclear complex, [{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5b**), was half of those of the corresponding bands for a dinuclear complex, [{(bzac)Pd(II)}$_2$(taet)] (**7a)**. As for the [{(npac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5c**), the intensity of the corresponding band was one-third of that of [{(npac)Pd(II)}$_2$(taet)] (**7b**). The results indicated that the electronic effects caused by the twisting of the two terminal benzyl or naphthyl groups well propagated through the molecular axis with little decay, even when they were separated by 3 nm in case of the tetranuclear complexes.

VCD measurements of dinulcear and tetranuclear Pd(II) complexes: The VCD was recorded on the dinuclear and tetranuclear Pd(II) complexes with a purpose of studying the elongation effects of a molecular axis on their vibrational chiral properties. The spectroscopy has been applied previously for various types of chiral metal complexes.[20-28] As far as our literature survey is concerned, there are few applications of multi-nuclear metal complexes with no asymmetric carbon.

Figure 5 shows the experimental IR and VCD spectra of [{(hfac)Pd(II)}$_2$(dabe)] (dabe =1,2-diacetyl-1,2-dibenzoylethanato) (**6**), [{(bzac)Pd(II)}$_2$(taet)] (**7a**) and [{(npac)Pd(II)}$_2$(taet)] (**7b**). The former compound was axially chiral due to the twisting of two phenyl groups in the bridging ligand (dabe^{2-}).[17] The two phenyl groups were separated by 0.35 nm. In contrast, the latter compounds were axially chiral due to the substituted moieties at the terminal positions. They were separated by 1.5 nm. For all these dimers, the VCD signals showed the mirror-image relation between the antipodal pairs, confirming the reliability of the spectra. The experimental IR and VCD spectra were compared with the DFT calculation on the basis. The calculated IR and VCD were shown in the supporting information. As shown by numbering the corresponded peaks, the calculated spectrum well reproduced the observed one. The assignment of VCD peaks is summarized in Table S1(a)-(c) (supporting information). In [{(hfac)Pd(II)}$_2$(dabe)] (**6**), the stretching vibration of bridging dabe ligands are observed at the mirror-image in 1300-1450 cm^{-1}. On the other hand, in case of [{(bzac)Pd(II)}$_2$(taet)] (**7a**) and [{(npac)Pd(II)}$_2$(taet)] (**7b**), only terminal unsymmetrical C-C-C stretching was clearly observed around 1500 cm^{-1}.

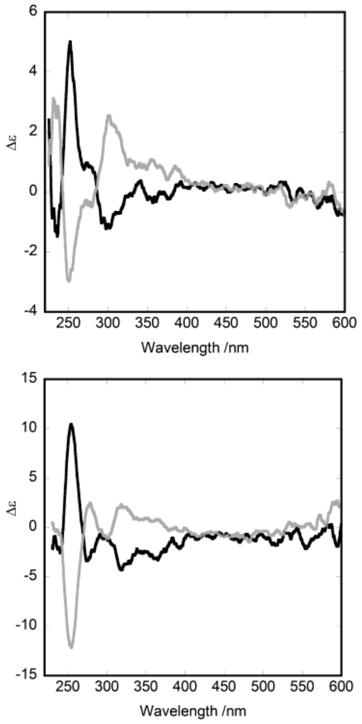

Figure 4. The ECD spectra of [{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5b**) (upper) and [{(npac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5c**) (lower) resolved on a chiral column. The solid and grey lines indicated the less and more retaining fractions, respectively. The solvent was dichloromethane.

Notably the magnitude of $\Delta\varepsilon$ was of the same order among these three compounds (i.e. 0.05, 0.1 and 0.15 for the peak at the most intense peaks in case of [{(hfac)Pd(II)}$_2$(dabe)] (**6**), [{(bzac)Pd(II)}$_2$(taet)] (**7a**) and [{(npac)Pd(II)}$_2$(taet)] (**7b**), respectively). The results indicated that the chiral nature caused by the vertical twisting of substituted groups propagated along the molecular axis beyond two Pd(II) units. As for the absolute configuration, the less and more retaining fractions were concluded to contain *R*- and *S*-isomers in case of [{(bzac)Pd(II)}$_2$(taet)] (**7a**) and [{(npac)Pd(II)}$_2$(taet)] (**7b**), respectively.

The VCD measurements were performed for tetranuclear complexes, [{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5b**) and [{(npac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5c**). No VCD peaks were, however, detected under the similar experimental conditions. The results implied that the chiral nature of molecular vibrations was unable to go beyond three Pd(II) units.

The situations were in contrast with the appearance of ECD for the same complexes. In other words, the vibrational chirality decayed more rapidly than the electronic ones. Presently the improvement of the machine with higher sensitivity is now under progress.

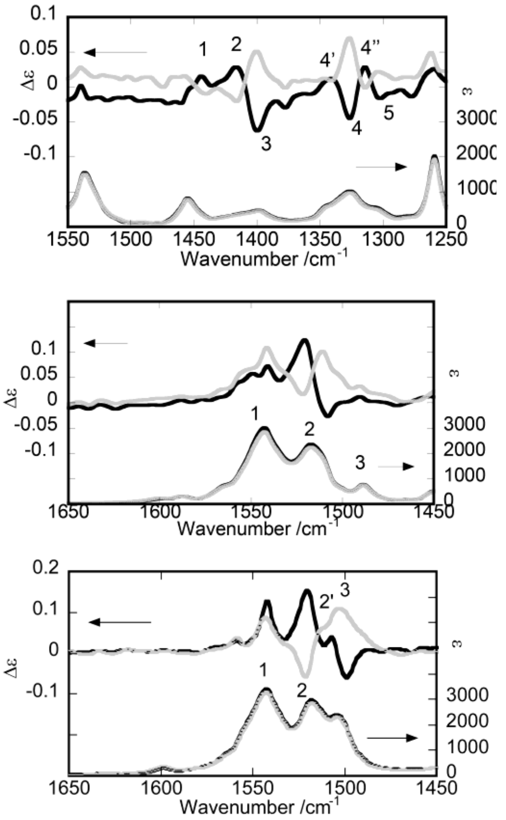

Figure 5. The experimental VCD spectra of the less retaining fraction (solid line) and the more retaining fraction (grey line) of [{(hfac)Pd(II)}$_2$(dabe)] (**6**) (upper) [{(bzac)Pd(II)}$_2$(taet)] (**7a**) (middle) and [{(npac)Pd(II)}$_2$(taet)] (**7b**) (lower) resolved on the chiral column. The solvent was CDCl$_3$. Correction was made to exclude the contribution of solvents from IR spectra.

Experimental

Syntheses of tetranuclear complexes

[{(hfac)Pd(II)}$_2$(tpret)] (1): The complex was synthesized according to the procedure reported previously. [17]

[{(taetH)Pd(II)}$_2$(tpret)] (2): To a dichloromethane (25 mL) solution of [{(hfac)Pd(II)}$_2$(tpret)] (211.0 mg, 0.24 mmol) and taetH$_2$ (237.5 mg, 1.32 mmol) was added dropwise triethylamine (182 µL, 1.32 mmol) at 0-5 °C, and the mixture was stirred at room temperature for 2.5 hours. After evaporation, the residue was treated with a limited amount of ethanol to give a yellow powder, which was purified by silica gel flash chromatography (chloroform) and HPLC on silica gel column (4 mm (i.d.) × 25 cm; GL Science, Japan, 2% methanol-dichloromethane) to afford [{(taetH)Pd(II)}$_2$(tpret)] in 17% yield.

[{(hfac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (4): A dichloromethane (3 mL) solution of [{(taetH)Pd(II)}$_2$(tpret)] (13.1 mg, 0.015 mmol) and [{(hfac)Pd(II)}$_2$(µ-OMe)] (13.7 mg, 0.020 mmol) was stirred for three days at room temperature. After removal of volatile materials, the residue was washed with hexane and dried in vacuo to give [{(hfac)Pd(II)(taet)Pd(II)}$_2$(tpret)]. The product was used without further purification.

[{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (5b): To a dichloromethane (2 mL) solution of [{(hfac)Pd(II) (taet)Pd(II)}$_2$(tpret)] obtained above and bzacH (7.3 mg, 0.045 mmol) was added dropwise triethylamine (9 µL, 0.06 mmol) and the mixture was stirred for 2.5 hours at room temperature. After evaporation, the residue was purified by silica gel flash chromatography (chloroform) and HPLC using silica gel column (0.8% methanol-dichloromethane) to give [{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)] in 73% yield.

[{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (5b). ^{1}H NMR (500 MHz, CDCl$_3$): δ=7.83 (4H, broad d, *J*=7.5 Hz, *o*-H), 7.47 (2H, broad t, *J*=7.5 Hz, *p*-H), 7.38 (4H, t, *J*=7.5 Hz, *m*-H), 6.06 (2H, s, CH), 2.20 (6H, s, CH$_3$), 2.15 (8H, q, *J*=7.5 Hz, CH$_2$), 1.973 (6H, s, CH$_3$), 1.969 (6H, s, CH$_3$), 1.96 (12H, s, CH$_3$), 1.02 ppm (12H, t, *J*=7.5 Hz, CH$_3$); ^{13}C NMR (125 MHz, CDCl$_3$): δ=190.5 (twice in integral ratio to signals of other carbonyl carbon atoms, C$_{\mathrm{CO}}$), 188.9 (C$_{\mathrm{CO}}$), 188.0 (C$_{\mathrm{CO}}$), 187.9 (twice, C$_{\mathrm{CO}}$), 187.6 (C$_{\mathrm{CO}}$), 180.5 (C$_{\mathrm{CO}}$), 135.9 (C$_{\mathrm{arom}}$), 131.5 (C$_{\mathrm{arom}}$), 128.3 (*o*-C$_{\mathrm{arom}}$), 127.5 (*m*-C$_{\mathrm{arom}}$), 112.1 (twice, C$_{\mathrm{vinyl}}$), 110.1 (C$_{\mathrm{vinyl}}$), 98.6 (C$_{\mathrm{vinyl}}$), 31.5 (C$_{\mathrm{methylene}}$), 26.21 (twice, C$_{\mathrm{methyl}}$), 26.17 (C$_{\mathrm{methyl}}$), 26.09 (C$_{\mathrm{methyl}}$), 26.01 (C$_{\mathrm{methyl}}$), 9.9 (C$_{\mathrm{methyl\ in\ Et}}$) ppm; HRMS (ESI$^+$, CH$_3CN/H_2$O) calcd for $C_{54}H_{62}O_{16}Pd_4$+H$^+$ 1391.0286, found *m*/*z*=1391.0299 [M+H$^+$].

Tetranuclear complexes [{(dbm)Pd(II)(taet)Pd(II)}$_2$(tpret)] **(5a)** and [{(npac)Pd(II)(taet)Pd(II)}$_2$(tpret)] **(5c)** were synthesized in a similar manner as above by the respective use of dbmH and npacH.

Dinuclear complexes [{(hfac)Pd(II)}$_2$(dabe)] (**6**) and [{(bzac)Pd(II)}$_2$(taet)] (**7a**) were reported in the previous paper. [17] Dinuclear complex [{(npac)Pd(II)}$_2$(taet)] **(7b)** was synthesized in a manner similar to preparation of **7a**.

[{(npac)Pd(II)}$_2$(taet)] (7b). ^{1}H NMR (500 MHz, CDCl$_3$): δ=8.38 (2H, s, aromatic H$_1$), 7.91-7.81 (8H, aromatic H$_{3,4,5,8}$), 7.53 (2H, broad t, *J*=8.0 Hz , aromatic H$_6$), 7.49 (2H, broad t, *J*=8.0 Hz , aromatic H$_7$), 6.23 (2H, s, CH), 2.26 (6H, s, CH$_3$), 2.03 (6H, s, CH$_3$), 2.01 ppm (6H, s, CH$_3$); ^{13}C NMR (125 MHz, CDCl$_3$): δ=188.9 (C$_{\mathrm{CO}}$), 188.1 (C$_{\mathrm{CO}}$), 187.7 (C$_{\mathrm{CO}}$), 180.2 (C$_{\mathrm{CO}}$), 134.8 (C$_{\mathrm{arom}}$), 133.1 (C$_{\mathrm{arom}}$), 132.6 (C$_{\mathrm{arom}}$), 129.2 (C$_{\mathrm{arom}}$), 128.3 (C$_{\mathrm{arom}}$), 128.0 (C$_{\mathrm{arom}}$), 127.7 (C$_{\mathrm{arom}}$), 127.6 (C$_{\mathrm{arom}}$), 126.5 (C$_{\mathrm{arom}}$). 124.1 (C$_{\mathrm{arom}}$), 112.2 (C$_{\mathrm{vinyl}}$), 98.9 (C$_{\mathrm{vinyl}}$), 26.2 (C$_{\mathrm{methyl}}$), 26.1 (C$_{\mathrm{methyl}}$), 26.0 (C$_{\mathrm{methyl}}$) ppm; HRMS (FAB$^+$, 3-NBA) calcd for $C_{38}H_{34}O_8Pd_2$+H$^+$ 833.0406, found *m*/*z*=833.0433 [M+H].

Optical resolution of racemic tetranuclear and dinuclear complexes

Racemic tetranuclear complexes, [{(bzac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5b**) and [{(npac)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5c**), were resolved respectively on a chiral column (4 mm (i.d.) × 25 cm; CHIRALPACK IC, Daicel, Japan) with dichloromethane containing 0.07% methanol. The ECD spectra of enantiomers thus resolved were recorded. Some of the chromatograms are given in ESI†. Racemic dinuclear complexes, [{(hfac)Pd(II)}$_2$(dabe)] (**6**), [{(bzac)Pd(II)}$_2$(taet)] (**7a**) and [{(npac)Pd(II)}$_2$(taet)] **(7b),** were all optically resolved in the same way as was reported in the previous paper.[17]

X-Ray chrystallographic analyses

X-Ray diffraction analysis was performed using a Rigaku VariMax with a Saturn diffractometer using multilayer mirror monochromated Mo Kα radiation (λ = 0.71073 Å) at 100 ± 1 K. The crystals were mounted in cryoloops. Collection of the reflection intensities and determination of the cell parameters were performed using CrystalClear (Rigaku)[29] and CrysAlisPro (Rigaku Oxford Diffraction).[30] Data were corrected for Lorentz polarization and absorption effects. The structures were solved using SHELXT 2018/2[31] and expanded using the Fourier technique. All calculations were performed using the CrystalStructure crystallographic software package[32] and SHELXL-2018/3[33] was used for structure refinement. Data were validated using PLATON.[34] Single crystals of [{(dbm)Pd(II)(taet)Pd(II)}$_2$(tpret)] (**5a**) were prepared by evaporating a $C_6H_5CH_3/C_2H_5OH$ solution. Crystallographic data: $C_{64}H_{66}O_{16}Pd_4{\cdot}2(C_7H_8)$, formula weight 1701.04, triclinic, *P*-1, a = 13.9277(3) Å, b = 14.8370(3) Å, c = 19.9949(4) Å, α = 104.707(2)°, β = 100.001(2)°, γ = 108.914(2)°, V = 3629.76(16) Å^3, Z = 2, T = 100 K, λ = 0.71073 Å, μ = 1.042 mm^{-1}. R_1 = 0.0499 ($I > 2\sigma(I)$), wR_2 = 0.1026 (all data), GOF = 1.025 ($I > 2\sigma(I)$), CCDC No. 1910079. Single crystals of [{(npac)Pd(II)}$_2$(taet)] (**7b**) were obtained by recrystallization from 1,2-dichloroethane/*n*-hexane. Crystallographic data: $C_{38}H_{34}O_8Pd_2{\cdot}C_2H_2Cl_4$, formula weight: 999.29, $P2_1/c$, a = 21.4114(6) Å, b = 16.1953(4) Å, c = 11.4025(2) Å, α = 90°, β = 94.113(2)°, γ = 90° V = 3943.79(16) Å^3, Z = 4, T = 100 K, λ = 0.71073 Å, μ = 1.235 mm^{-1}. R = 0.0420 ($I > 2\sigma(I)$), wR_2 = 0.0900 (all data), GOF = 1.023 ($I > 2\sigma(I)$), CCDC No.1910080.

Instrumentation: NMR spectra were obtained using a spectrometer, AVIII500 (Bruker). UV-visible electronic spectra were recorded with UV-vis spectrophotometer (U-2810, Hitachi Ltd., Japan). Circular dichroism spectra were measured with a polarimeter (J-720, Jasco, Japan).

Spectroscopic measurements: The VCD spectra were measured with a machine developed in our laboratory with corporation of JASCO Co. Ltd., Japan (PRESTO-S-2016 VCD/LD spectrometer).[27] The machine was a concurrent system in combination with linear dichroism. The machine is the single PEM system. The calibration was made by use of a quarter wave-retardation and an analyser. A $CDCl_3$ solution of the complex (ca.0.02 M) was injected into a cell (200 μm in optical length) with BaF_2 windows. The signal was accumulated during 10000 scans for each complex. The resolution of wavenumber was 4 cm^{-1}. The baseline correction was performed for the IR spectra by subtracting the solvent contribution.

Computational details

The VCD and IR of Pd(II) complexes were theoretically calculated by use of Gaussian 16 program or Gaussian 09 program.[35] Geometry optimization was performed at the DFT level (B3LYP functional with Stuttgart ECP for Pd(II) and 6-31G(d,p) for the other atoms) in the ground states. The VCD intensities were determined by the vibrational rotational strength and the magnetic dipole moments, which were calculated by the magnetic field perturbation (MFP) theory formulated using magnetic field gauge-invariant atomic orbitals. The calculated intensities were converted to Lorentzian bands with 4 cm^{-1} half-width at half-height. The observed spectra were assigned on the basis of animations of the molecular vibration with Gauss view 6.0 (Gaussian Inc.).

Conclusions

Tetranulcear and dinuclear square planar Pd(II) complexes were prepared by use of bis-β-diketonato ligands. These complexes were axially chiral due to the vertical twisting of the β-diketonato moieties. The present work provides a way to introduce axial chirality to achiral square planar moieties. The present strategy is simpler and can be a benchmark for developing the chiral tectonics of polymeric square planar Pd(II) complexes with axial chirality.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The acknowledgements come at the end of an article after the conclusions and before the notes and references.
This work was financially supported by the JSPS KAKENHI Grant-in-Aid for Scientific Research (B) JP17H03044 and JST MIRAI grants (JPMJMI18GC). The computations were performed using the Research Center for Computational Science, Okazaki, Japan.

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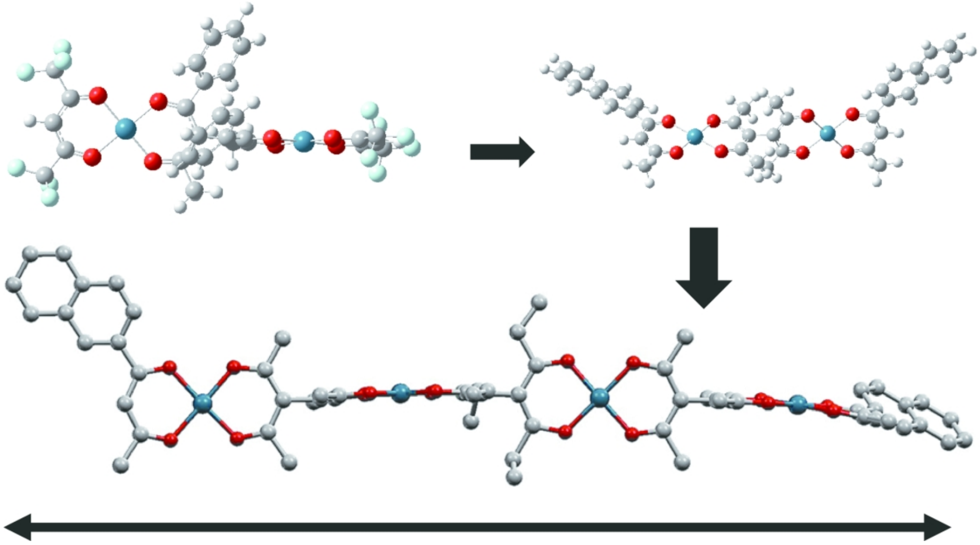
Tetranuclear Pd(II)complexes were synthesized according to the molecular tectonics approach. It was focused how the elongation of a molecular axis affected the chiro-optical properties of a molecule with axial chirality.



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