

Supporting Information for

Effects of Auxiliary Ligands of Pd(II) Dimers on Induction of Chiral Nematic Phases: Chirality Inversion and Photo-responsive Structural Change

Kenji Tamura,^a Jun Yoshida,^b Masahiro Taniguchi,^c Takafumi Kitazawa,^d Akihiko Yamagishi^d and Hisako Sato^{e*}

^aNational Institute of Materials Science, Tsukuba 305-0044, Japan,

^bDepartment of Chemistry, Kitasato University, Kanagawa 112-8610, Japan.

^cKanazawa Institute of Technology, Kanazawa 921-8501, Japan

^dSchool of Science, Toho University, Funabashi Chiba 274-851, Japan

^eGraduate School of Science and Engineering, Ehime University, Matsuyama 790-8577, Japan, Fax: +81-89-927-9599; Tel: +81-89-927-9599; E-mail: sato.hisako.my@ehime-u.ac.jp

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S1. The ^1H NMR spectra (400 MHz, CDCl_3) and mass analyses of Pd complexes

The data of chemical shift and molecular mass are given for the Pd(II) complexes prepared in the present work:

[{Pd(II)(acac)}₂(baet)]. $\delta = 5.44$ (2H, s, CH), 2.20 (2H, m, CH), 2.10 (12H, s, CH₃), 1.96 (6H, s, CH₃), 2.04 (4H, d, CH₂), 0.89 (12H, m, CH₃); $m/z = 346$ (calc. 346.7 for $\text{C}_{26}\text{H}_{38}\text{O}_8^{106}\text{Pd}^{107}\text{Pd}$).

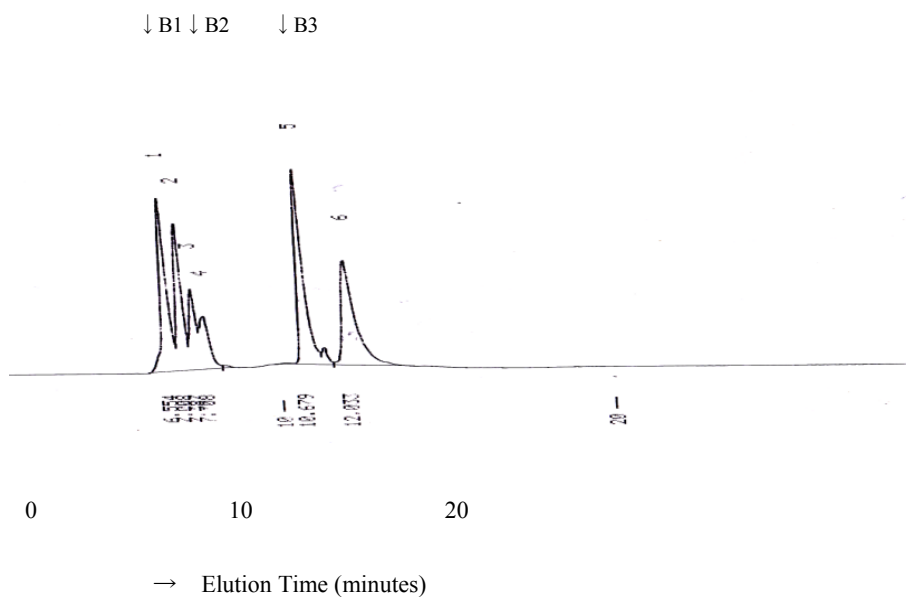
[{Pd(II)(dbm)}₂(baet)]. $\delta = 7.94$ (8H, d, aromatic), 7.53 (4H, t, aromatic), 7.46 (8H, t, aromatic), 6.76 (2H, s, CH), 2.28 (2H, m, CH), 2.19 (4H, d, CH₂), 2.05 (6H, s, COCH₃), 0.96 (12H, m, CH₃); $m/z = 939$ (calc. 939.8 for $\text{C}_{46}\text{H}_{46}\text{O}_8^{106}\text{Pd}^{107}\text{Pd}$).

[{Pd(II)(C₉-dbm)}₂(baet)]. $\delta = 7.92$ (8H, d, aromatic), 6.92 (8H, d, aromatic), 6.66 (2H, s, CH), 4.04 (8H, t, CH₂), 2.28 (2H, m, CH), 2.19 (4H, d, CH₂), 2.05 (6H, s, COCH₃), 1.34 (80H, m, CH₂), 0.96 (12H, m, CH₃), 0.90 (12H, m, CH₃); $m/z = 1508$ (calc. 1508.8 for $\text{C}_{82}\text{H}_{118}\text{O}_{12}^{106}\text{Pd}^{107}\text{Pd}$).

[{Pd(II)(C₈-azoacac)}₂(baet)]. $\delta = 7.95$ (8H, d, aromatic), 7.90 (8H, d, aromatic), 7.30 (8H, d, aromatic), 7.03 (8H, d, aromatic), 4.05 (8H, t, CH₂), 2.22 (2H, m, CH), 1.90 (12H, s, CH₃), 2.19 (4H, d, CH₂), 2.01 (6H, s, COCH₃), 1.34 (48H, m, CH₂), 0.92 (24, m, CH₃); $m/z = 1309$ (calc. 1309.4 for $\text{C}_{66}\text{H}_{87}\text{N}_4\text{O}_{10}^{106}\text{Pd}^{107}\text{Pd}$).

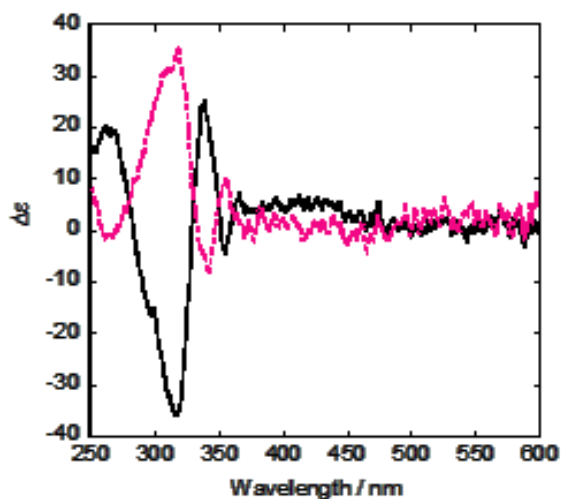
S2. An example of the chromatographic resolution of Pd(II) complexes

The following is an example of chromatographic resolution in case of a mixture of *cis*- and *trans*-[Pd(C₈-azoacac)]₂(baet).



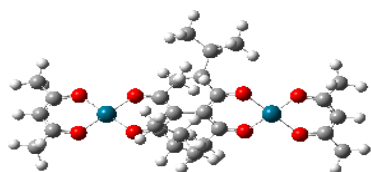
The chromatogram when a dichloromethane solution of [Pd(C₈-azoacac)]₂(baet) was eluted on a chiral column (Chiral Pack CI (Daicel, Japan: 0.4 cm (i.d.) × 25 cm)). Dichloromethane was flowed at a rate of 1.0 ml/min. The elution was monitored at 430 nm. The sample solution was irradiated at 460 nm before elution to give a mixture of *cis*- and *trans*-isomers. The doublet peaks at B1, B2 and B3 corresponded to the enantiomeric pairs of *trans*-, *trans*-/*cis*- and *cis*-isomers, respectively.

S3. The CD spectra of the resolved Pd(II) complexes



The CD spectra of the first (black) and second (red) fractions when a racemic mixture of *trans*-[Pd(C₈-azoacac)₂(baet)] was resolved on a chiral column. . [Pd(C₉-dbm)₂(baet)] and *cis*-[Pd(C₈-azoacac)₂(baet)] gave nearly the same spectra.

S4. DFT calculation of UV-vis and CD spectra of $[\{\text{Pd}(\text{acac})\}_2(\text{baet})]$



A molecular model of $[\{\text{Pd}(\text{II})(\text{acac})\}_2(\text{baet})]$

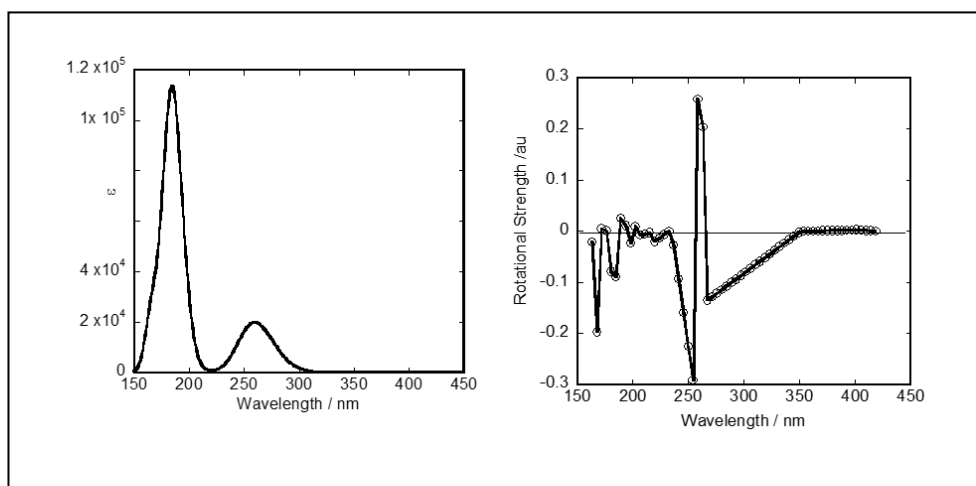


Figure S4. Calculated UV-vis (left) and CD (right) spectra of $[\{\text{Pd}(\text{II})(\text{acac})\}_2(\text{baet})]$

S5. The microscope image of the texture of a liquid crystal sample

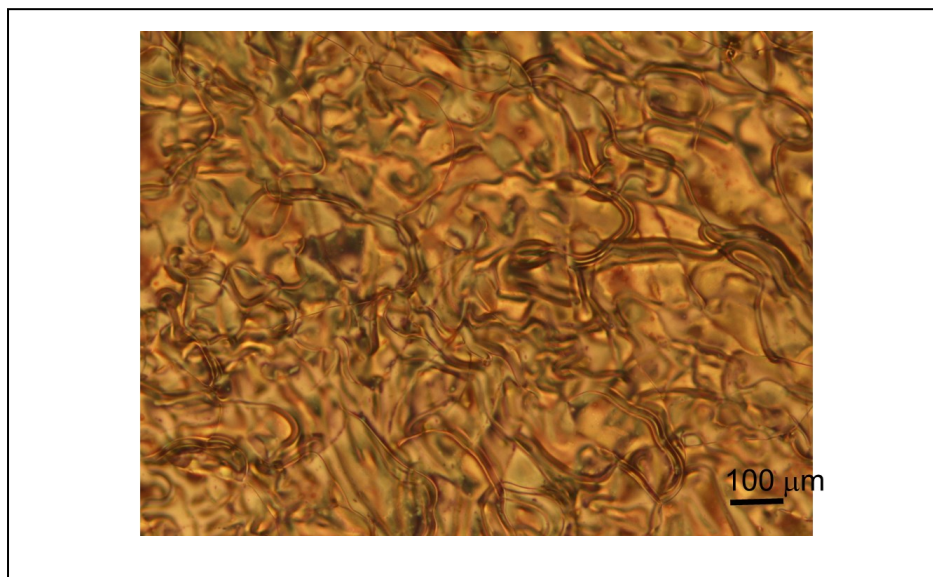


Figure S5. The cross-nicoled microscopic image of a liquid crystal sample. The sample (MBBA doped with $[\text{Pd(II)(dbm)}_2(\text{baet})]$ at the molar ratio of 0.3 %) was sandwiched between two glass plates. Temperature was 25 °C. The sample transformed into an isotropic media (dark image) at 39.6 ± 0.2 °C

S6. The microscope image of a liquid crystal sample mounted in Cano wedge

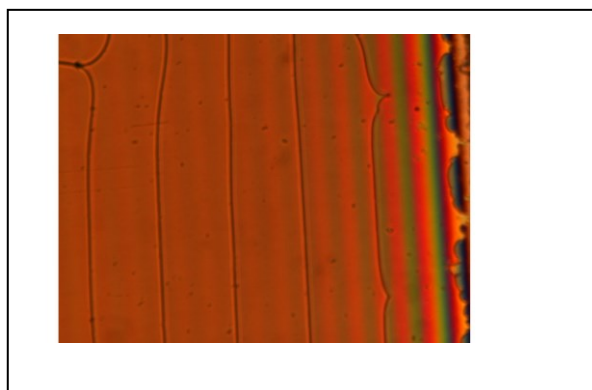


Figure S6. The microscopic image of a liquid crystal sample injected into a Cano wedge. The sample (MBBA doped with $[\text{Pd(II)(dbm)}_2(\text{baet})]$ at the molar ratio of 0.3 %) was into a Cano wedge at 50 °C and cooled to room temperature. The lines locating with the regular spacing were defect lines, indicating the formation of a chiral nematic phase (N^*).

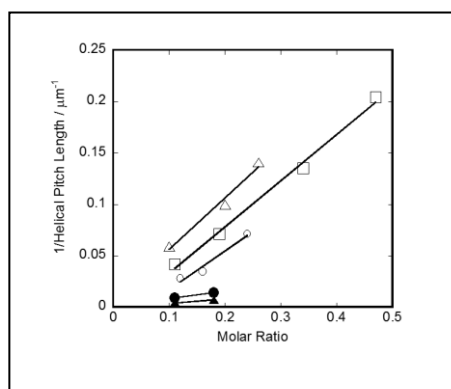
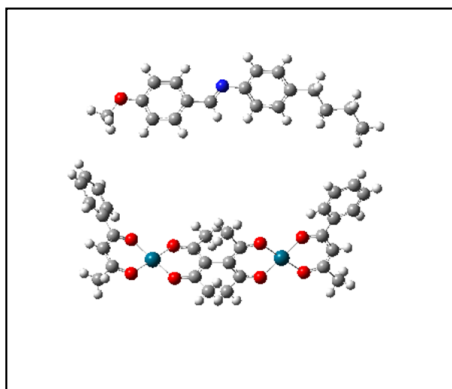


Figure S6 (b). The dependence of the inverse of helical pitch length (p) on the molar ratio of a dopant (x). The samples were following: R - $[\text{Pd}(\text{acac})_2(\text{baet})]$ (open circle), R - $[\text{Pd}(\text{dbm})_2(\text{baet})]$ (open square), R - $[\text{Pd}(\text{C}_9\text{-dbm})_2(\text{baet})]$ (open triangle), $\text{trans-}R$ - $[\text{Pd}(\text{C}_8\text{-dbm})_2(\text{baet})]$ (solid circle) and $\text{cis-}R$ - $[\text{Pd}(\text{C}_8\text{-dbm})_2(\text{baet})]$ (solid triangle).

S7. The comparison of the molecular sizes of MBBA and [$\text{Pd(II)(phac)}_2(\text{taet})$]



The molecular size is compared between MBBA and [$\text{Pd(II)(phac)}_2(\text{taet})$], showing that their molecular length is nearly equal (~ 1.5 nm).

S8. The crystal data and the table of bond lengths and angles

Table S8 (a). Crystallographic data for [$\{\text{Pd(II)(acac)}_2\}$ (baet)].

Compound	[$\{\text{Pd(II)(acac)}_2\}$(baet)]
Formula	C ₂₆ H ₃₈ O ₈ Pd ₂
Formula weight	691.36
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> / Å	11.1943 (10)
<i>b</i> / Å	21.6804 (19)
<i>c</i> / Å	11.8179 (10)
β / °	98.940 (1)
<i>V</i> / Å ³	2833.3 (4)
<i>Z</i>	4
<i>T</i> / K	120
<i>D</i> _x / Mg m ⁻³	1.621
Dimensions / mm	0.52, 0.44, 0.26
μ (Mo-K α) / mm ⁻¹	1.31
F(000)	1400
Reflections collected	31569
Unique reflections	6506
Reflections with <i>I</i> > 2 σ (<i>I</i>)	6075
Parameters	335
GOF on F ²	1.16
^a <i>R</i> ₁ [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.028
^b <i>wR</i> ₂ (all data)	0.065

$${}^a R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|, {}^b wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$$

Table S8 (b). Selected bond lengths and angles (numbering is shown in the figure below)

Pd-O (Å)	C-C (Å)	O-Pd-O (°)	C-C-C-C (°)
Pd1—O1 1.980 (2)	C10—C11 1.413 (3)	O1—Pd1—O2 94.63 (8)	C10—C11—C16—C15 92.4 (3)
Pd1—O2 1.987 (2)	C11—C12 1.419 (3)	O3—Pd1—O4 93.01 (7)	
Pd1—O3 1.964 (2)	C11—C16 1.509 (3)	O5—Pd2—O6 92.90 (7)	
Pd1—O4 1.966 (2)	C15—C16 1.415 (3)	O7—Pd2—O8 94.78 (8)	
Pd2—O5 1.985 (2)	C16—C17 1.408 (4)		
Pd2—O6 1.973 (2)			
Pd2—O7 1.990 (2)			
Pd2—O8 1.986 (2)			

