Supporting Information for

Crystallization Induced Chiral Locking of a Central Labile Core in a Star-shaped Tetra-nuclear Complex

Hisako Sato,[a,b] **Yuka Furuno**[c]**, Yutaka Fukuda**[c]**, Kentaro Okamoto**[c] **and Akihiko Yamagishi**[c*]

[a,b] *The University of Tokyo, Tokyo, Japan and PRESTO, JST,Japan Fax: +81-3-5841-4019; Tel: +81-3-5841-4019; E-mail: h-sato@eps.u-tokyo.ac.jp*
[c] *Ochanomizu University, Tokyo, Japan. Fax: +81-3-5978-5575; Tel: +81-3-5978-5575; E-mail: yamagishi.akihiko@ocha.ac.jp*

* Prof. Akihiko Yamagishi

Department of Chemistry, Ochanomizu University, Tokyo 112-8610, Japan

Tel: +81-3-5978-5575

Fax: +81-3-5978-5575

e-mail:yamagishi.akihiko@ocha.ac.jp

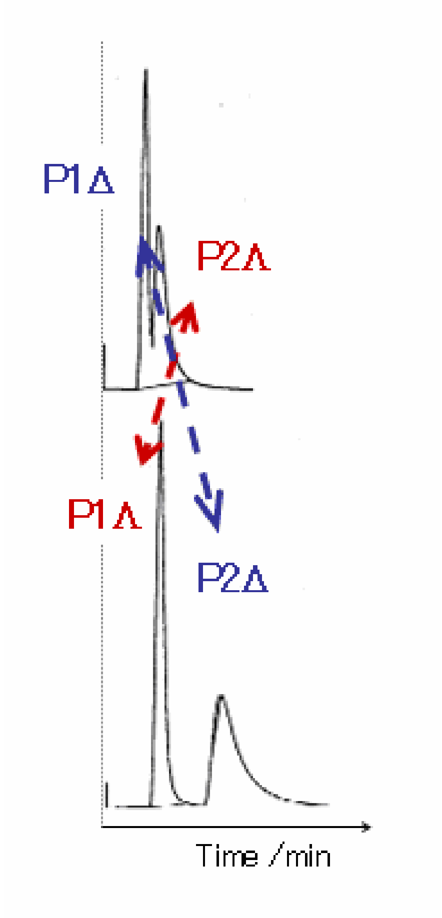
Syntheses of [Ru(III)(acac)$_2$(taetH)]: The complex was prepared by refluxing [Ru(III)(acac)$_2$(CH$_3$CN)$_2$]PF$_6$ (0.37 g, 0.70 mmol) and tetraacetylethane (tatetH$_2$) (0.14 g, 0.70 mmol) in toluene (120 mL) for 17 hours. The crude product was purified by being eluted with 1:10 (v/v) acetonitrile/benzene on a silica gel column. The compound was identified by mass spectra (m/z = 497 (obs.), 496.49 (calc.)), elemental analyses (Found: C, 48.22; H, 5.41. Calc. for RuC$_{20}$H$_{27}$O$_8$: C, 48.38; H, 5.48%) and ^{1}H nmr spectra (δ_H (250 MHz; CDCl$_3$; Me$_4$Si) 15.8 (1H, OH proton in taetH), 1.67 (6H,CH$_3$ protons in taetH), -4.32 (6H, CH$_3$ protons in acac), -7.33 (6H, CH$_3$ protons in acac), -7.83 (6H, CH$_3$ protons in taetH) and -31.81 (2H, CH protons in acac).

Spectroscopic measurements: Electronic absorption and circular dichroism spectra were measured with a U-2810 spectrophotometer (Hitachi, Japan) and a J-720 spectropolarimater (JASCO, Japan), respectively. XRD patterns were recorded on a RINT2100S X-ray diffractometer (Rigaku, Japan).

Complete list of reference (8): (8) Fisch, M. J.; Trucks,G. W.; Schlegel, H. B.; Scuseria,G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, Jr. T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A. ; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R. ; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P.Y.; Morokuma, K.; Voth, G.A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B. ; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C.Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W. ;

Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

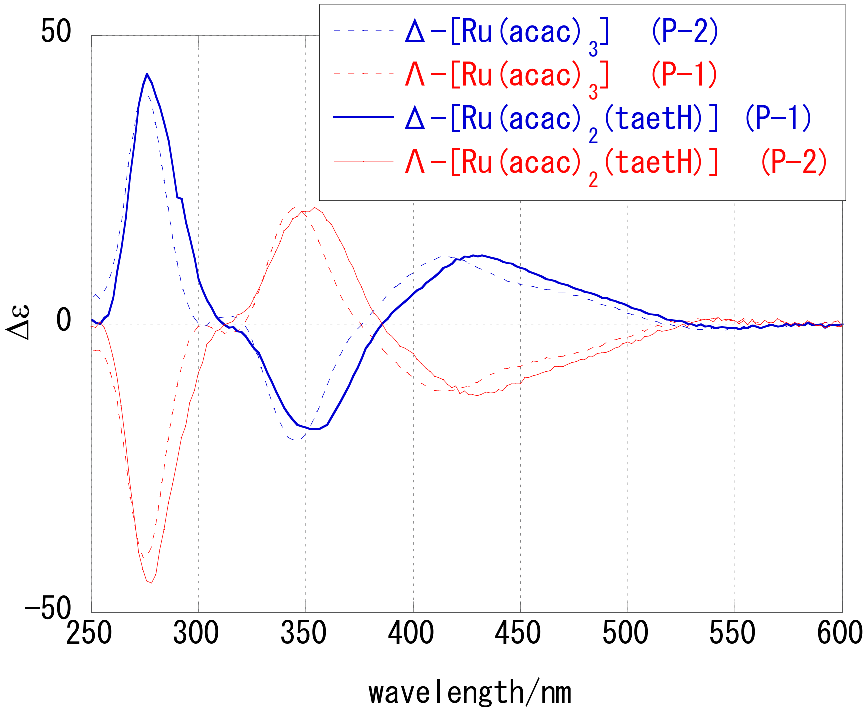
Chromatograms in HPLC separation: The chromatographic results are shown below when [Ru(III)(acac)$_2$(taetH)] (upper) and [Ru(III)(acac)$_3$] (lower) were eluted with 10:1 methanol/chloroform on a chiral column (25 cm×4 mm (i.d.); Ceramosphere RU-1, Shiseido Co.) The column was packed with an ion-exchange adduct of Δ-[Ru(II)(phen)$_3$]$^{2+}$ and synthetic hectorite: flow rate =1 mL min^{-1} , monitoring wavelength = 500 nm and temperature = 40 ℃.



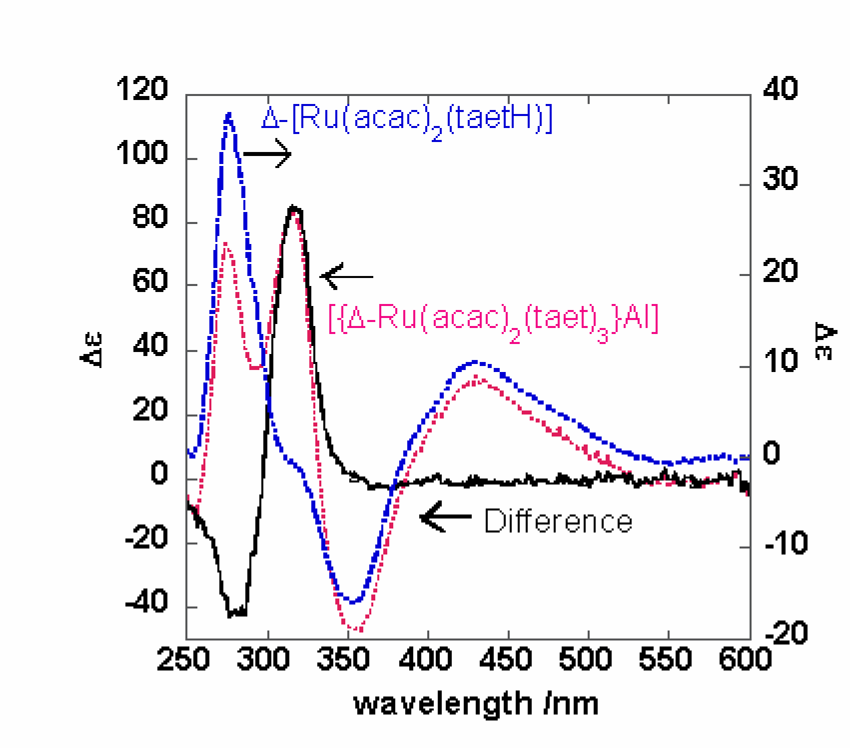
[Ru(III)(acac)$_2$(taetH)]

[Ru(III)(acac)$_3$]

Circular dichroism (CD) spectra of resolved enantiomers: The CD spectra of methanol solutions of [Ru(III)(acac)$_2$(taetH)) (red) and [Ru(III)(acac)$_3$] (blue) are shown below, where P1 and P2 are the first and second fractions during chromatographic resolution, respectively.



Circular dichroism (CD) spectra of Δ-[Ru(III)(acac)$_2$(taetH)] and, [{Δ-Ru(III)(acac)$_2$(taet)}$_3$Al(III)]: The CD spectra of Δ-[Ru(III)(acac)$_2$(taetH)] (blue) and [{Δ-Ru(III)(acac)$_2$(taet)}$_3$Al(III)] (pink) are shown below. The difference spectrum between these two spectra is shown by the black curve, in which Δε of Δ-[Ru(III)(acac)$_2$(taetH)] is multiplied by three.



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The UV spectra of metal complexes: The electronic absorption spectra of methanol solutions of [Ru(III)(acac)$_3$] (red), [Ru(III)(acac)$_2$(taetH)] (orange), [{Ru(III)(acac)$_2$(taet)}$_3$Fe(III)] (black) and [{Ru(III)(acac)$_2$(taet)}$_3$Al(III)] (blue) in methanol are shown below. [{Ru(III)(acac)$_3$(taet)}$_2$Pd(II)] gave the same spectrum as [Ru(III)(acac)$_2$(taetH)].

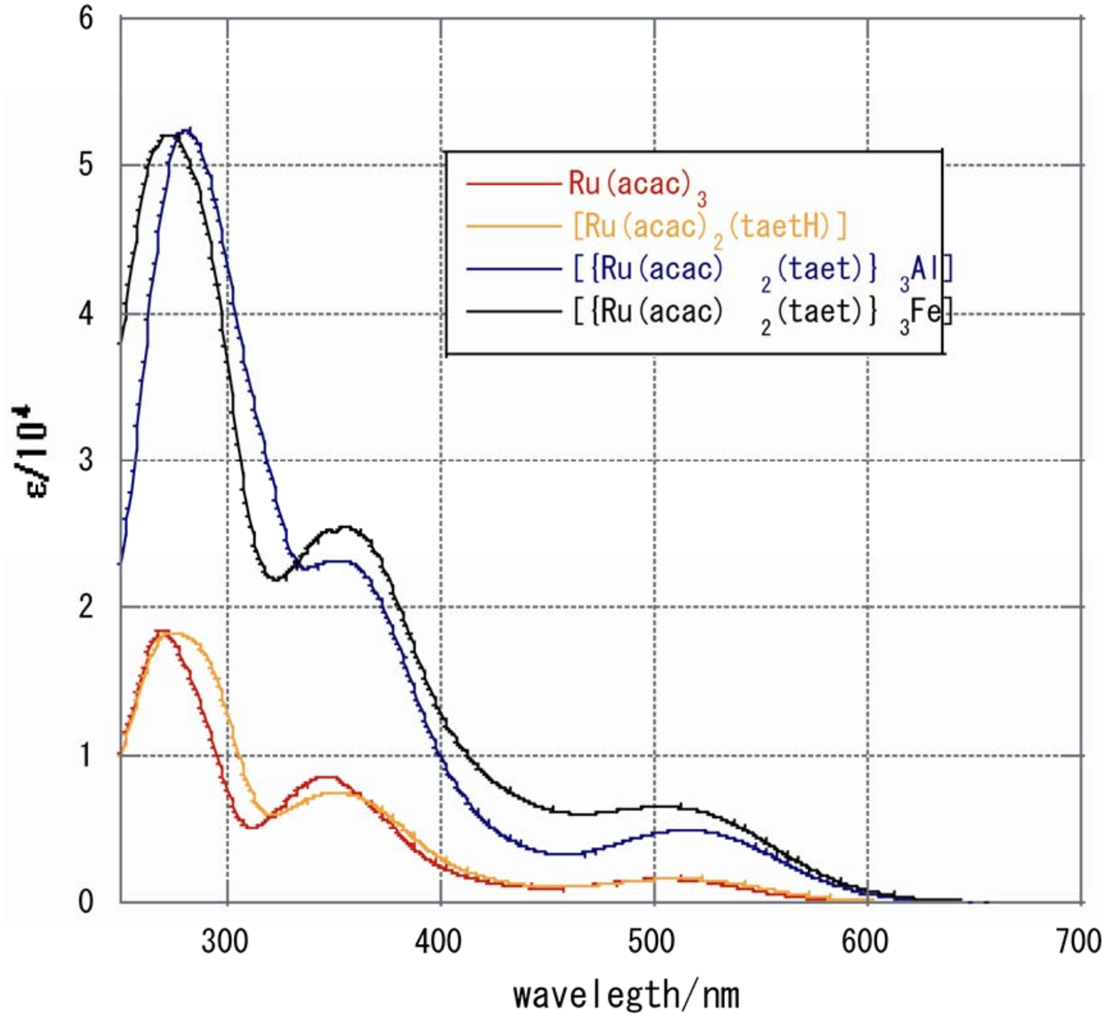


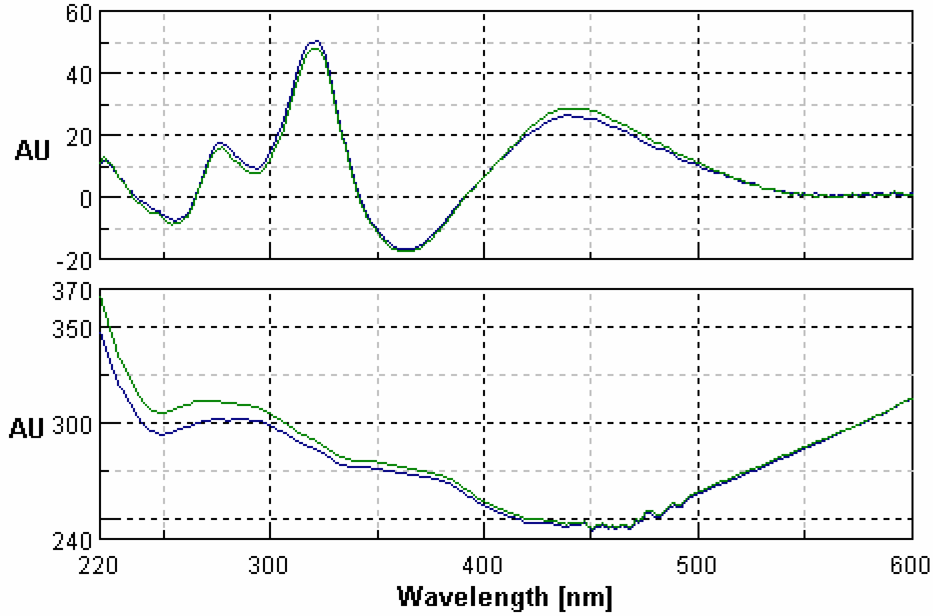
Table S1. FTIR, MS and elemental analysis data

Complex	$\nu_{C=O}$ /cm^{-1}	$\nu_{C=C}$ /cm^{-1}	λ_{max}/nm※ (ε)	FAB-MS (m^+/z) (calc.)	Elemental analysis / (obs.) % (calc.)	
					C	H
[Ru(III)(acac)$_2$(taetH)]	1544	1517	513 (1600)	497 M$^+$ (496.49)	48.22 (48.38)	5.41(5.48)
[{Ru(III)(acac)$_2$(taet)}$_2$ Pd(II)]	1541	1519	516	1098 M$^+$ (1097.4)	-	
[{Ru(III)(acac)$_2$(taet)}$_3$ Fe(III)]	1543	1517	505 (6500)	1544 M$^+$ (1542.3)	46.26 (46.73)	5.08(5.10)
[{Ru(III)(acac)$_2$(taet)}$_3$ Al(III)]	1547	1517	514 (4900)	1515 M$^+$ (1513.4)	46.76 (47.62)	5.29(5.19)

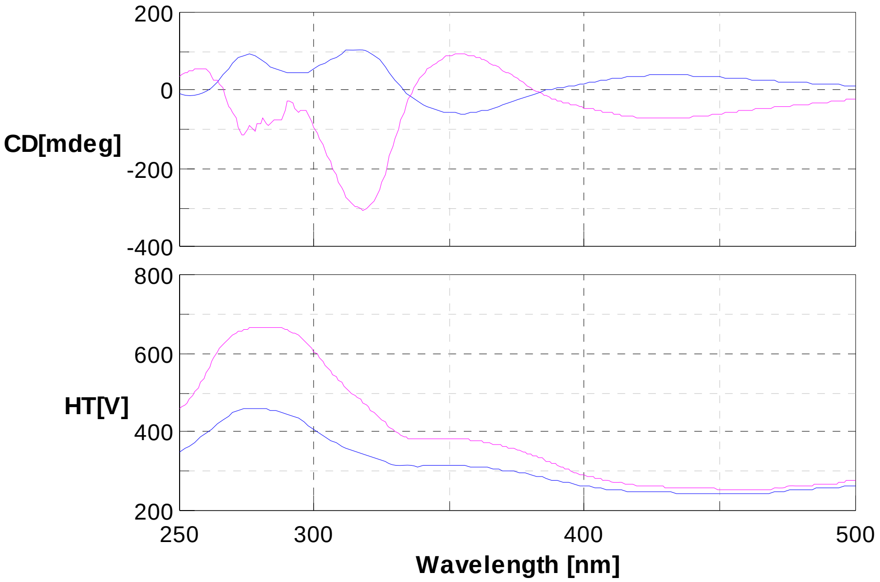
Table S2. NMR data

Complex	δ (ppm) -CH_3	δ (ppm) =CH-	δ (ppm) -OH
[Ru(III)(acac)$_2$(taetH)]	1.67 (6H) -4.32 (6H) -7.33 (6H) -7.83 (6H)	-31.81 (2H)	15.88 (1H)
[{Ru(III)(acac)$_2$(taet)}$_2$Pd(II)]	1.91 (12H) -3.82 (12H) -6.83 (12H) -8.43 (12H)	-30.49 (4H)	—
[{Ru(III)(acac)$_2$(taet)}$_3$Fe(III)]	-3.48 -6.40	-29.69	—
[{Ru(III)(acac)$_2$(taet)}$_3$Al(III)]	1.92 1.89 1.84 1.80 1.72 1.66 (18H) -3.20 -3.35 -3.46 -3.63 -3.77 (18H) -6.02 -6.41 -6.63 -6.77 (18H) -9.51 -9.63 -9.87 -9.98 -10.06 (18H)	-29.12 -29.70 -30.23	—
[{Δ-Ru(III)(acac)$_2$(taet)}$_3$Al(III)]	-3.32 (18H) -6.28 (18H) -9.16 (18H)	-29.36	

The CD spectrum o f a powder sample of [{Δ-Ru(III)(acac)$_2$(taet)}$_3$Al(III)]: The CD spectrum of [{Δ-Ru(III)(acac)$_2$(taet)}$_3$Al(III)] in a solid sate is shown below, in which the sample was prepared by casting a freshly prepared chloroform solution of the compound onto a quartz glass. The spectrum was measured at the rotation angle of 0 and 90 degrees as shown by green and blue curves, respectively. No difference between these two curves confirmed that the measured spectrum was free from any dichroic effect.



The CD spectrum of [{Δ-Ru(III)(acac)$_2$(taet)}$_3$Al(III)] and [{Λ-Ru(III)(acac)$_2$(taet)}$_3$Al(III)]: The CD spectra of fresh solutions of [{Δ-Ru(III)(acac)$_2$(taet)}$_3$Al(III)] (blue) and [{Λ-Ru(III)(acac)$_2$(taet)}$_3$Al(III)] (pink) were measured as shown below. The positive (blue) and negative peaks (pink) around 320 nm confirmed the formation of Λ-[{Δ-Ru(III)(acac)$_2$(taet)}$_3$Al(III)] and Δ-[{Λ-Ru(III)(acac)$_2$(taet)}$_3$Al(III)], respectively.



The XRD patterns of Δ-[Ru(III)(acac)$_2$taeH)] and [{Δ-Ru(III)(acac)$_2$(taet)}$_3$Fe(III)]: The XRD patterns of Δ-[Ru(III)(acac)$_2$taetH] (upper) and [{Δ-Ru(III)(acac)$_2$(taet)}$_3$Fe(III)] (lower) were recorded on their powder samples (0.1 g) as shown below: wavelength 1.541 nm (CuKα).