

# Supporting Information for

## **Molecular Recognition of Star-burst Tetranuclear Ru(III) Complexes on a Chirally Modified Clay Surface**

**Noriko Fujimoto<sup>a</sup>, Yukie Mori<sup>a</sup>, Akihiko Yamagishi<sup>a</sup> and Hisako Sato,<sup>b,c\*</sup>**

<sup>a</sup>Faculty of Science, Ochanomizu University, Tokyo, 112-8610, Japan. <sup>b</sup> Graduate School of Science and Engineering, Department of Chemistry, Ehime University, Matsuyama, 790-8577, Japan. E-mail: [hsato@chem.sci.ehime-u.ac.jp](mailto:hsato@chem.sci.ehime-u.ac.jp)

<sup>c</sup> PRESTO, Japan Science and Technology Agency, Chiba, 277-8561, Japan.

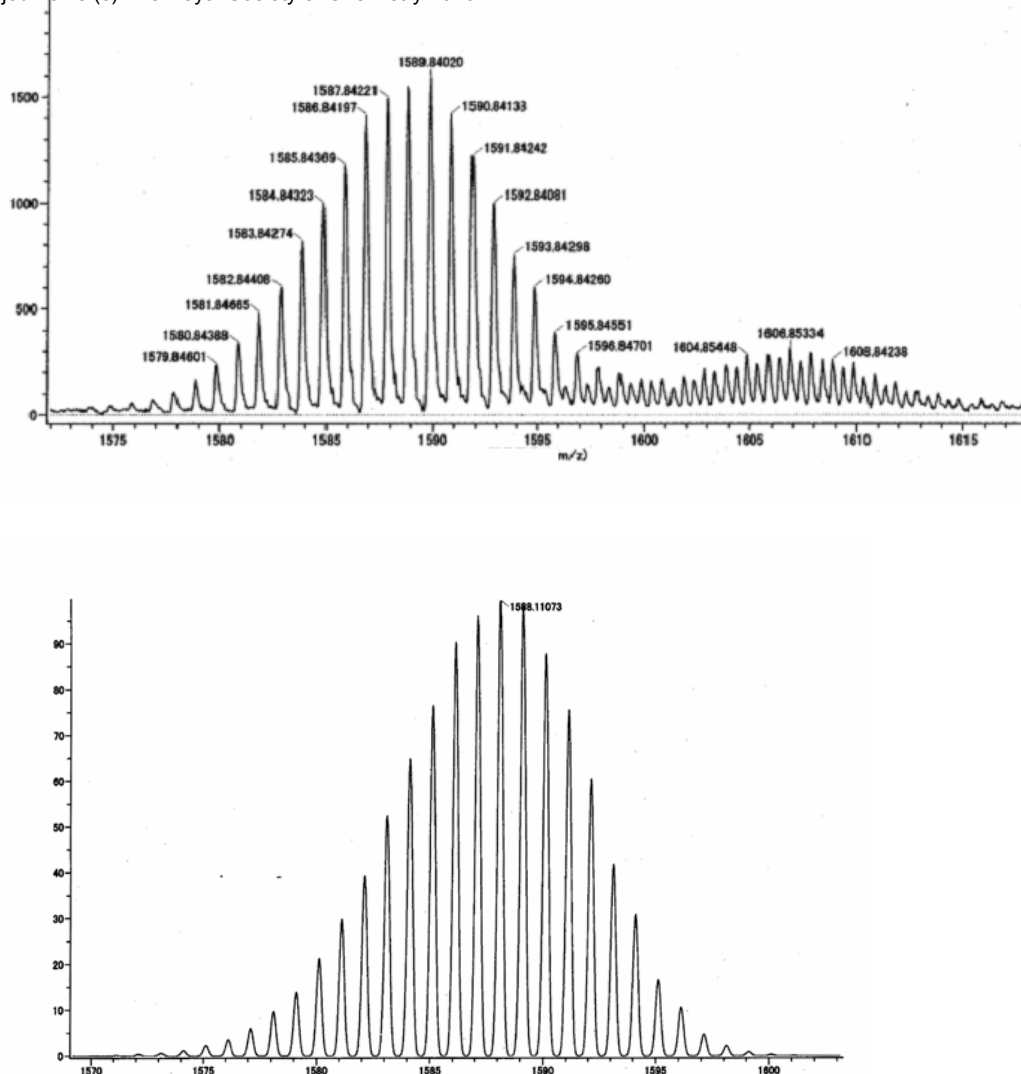
\* Prof. Hisako Sato

Department of Chemistry, Ehime University, Ehime 790-8577, Japan

Tel: +81-89-927-9599

Fax: +81-89-927-9599

e-mail: [hsato@chem.sci.ehime-u.ac.jp](mailto:hsato@chem.sci.ehime-u.ac.jp)



**Figure S1.** The observed (upper) and calculated (lower) MS spectra of tetranuclear Ru(III) complex: (m/z) obs: 1589.8 (calc. 1587.5). The upper spectrum was obtained by ESI technique with positive mode for the sample dissolved in an MeCN-water mixed solvent.

**$^1\text{H}$  NMR Data of  $[\text{Ru}(\text{acac})_2(\text{MeCN})_2]\text{PF}_6$  and  $[\text{Ru}(\text{taetH})_3]$  (400MHz,  $\text{CDCl}_3$ ):**

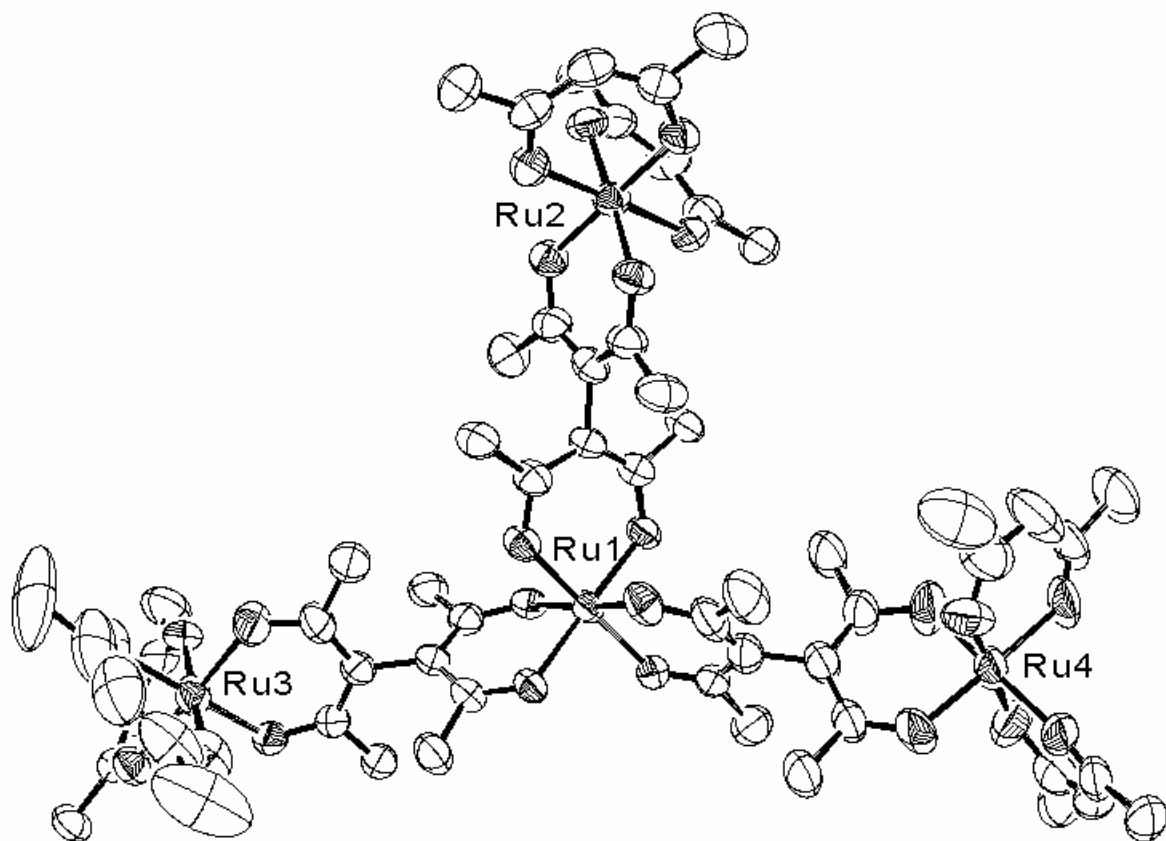
$[\text{Ru}(\text{acac})_2(\text{MeCN})_2]\text{PF}_6$

$\delta = -26.45$  (6H,  $\text{CH}_3$ ),  $-22.62$  (6H,  $\text{CH}_3$ ),  $37.09$  (6H,  $\text{CH}_3$ )

$[\text{Ru}(\text{taetH})_3]$

$\delta = -8.44$  (18H,  $\text{CH}_3$ ),  $2.02$  (18H,  $\text{CH}_3$ ),  $15.81$  (3H, OH)

(m/z) obs. 690.2 (calc. 692.7)



**Figure S2.** The ORTEP drawing of  $\Delta\text{-}\Lambda\Lambda\Delta\text{-}[\{\text{Ru(III)(acac)}_2(\text{taet})\}_3\text{Ru(III)}]$  in the crystal. H-atoms and solvent molecules are omitted for clarity. The thermal ellipsoids include 50% probability. In the minor component, Ru4 has  $\Lambda$ -configuration:  $\angle\text{Ru3-Ru1-Ru4} = 157.3^\circ$ ,  $\angle\text{Ru2-Ru1-Ru3} = 106.2^\circ$ , and  $\angle\text{Ru2-Ru1-Ru4} = 93.4^\circ$ .<sup>10</sup>

**Table S1.** Crystallographic Data

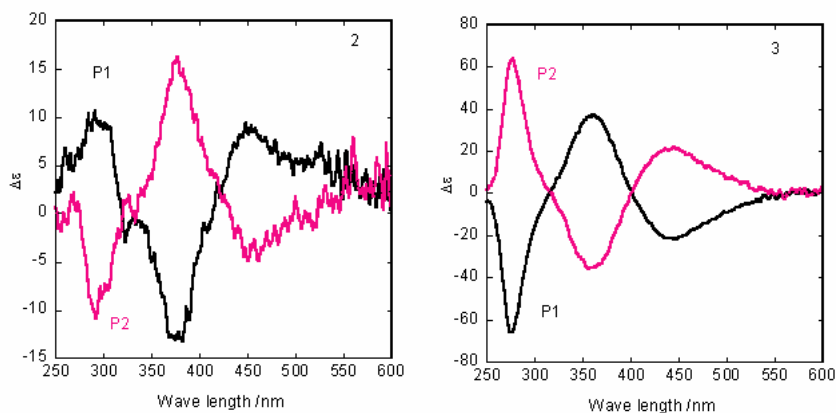
Formula	C <sub>60</sub> H <sub>84</sub> O <sub>27</sub> Ru <sub>4</sub>		
Molecular weight	1641.55	Crystal size / mm	0.25 × 0.07 × 0.05
<i>T</i> / K	90(2)	$\lambda$ / Å	0.71073
Crystal system	Monoclinic	$\mu$ / mm <sup>-1</sup>	0.798
Space Group	<i>C2/c</i>	Total reflections	148735
<i>a</i> / Å	27.9895(11)	Unique reflections	14270
<i>b</i> / Å	24.6831(8)	Observed reflections	9310
<i>c</i> / Å	23.4837(10)	<i>R</i> <sub>int</sub>	0.0985
$\beta$ / °	92.1100(10)	<i>R</i> <sub>1</sub> [ $F_0^2 > 2 \sigma(F_0^2)$ ]	0.0737
<i>V</i> / Å <sup>3</sup>	16213.1(11)	<i>wR</i> <sub>2</sub> (all data)	0.2375
<i>Z</i>	8	Goodness of fit	1.053
<i>D</i> <sub>calc</sub> / mg m <sup>-3</sup>	1.345	Reflection / Parameter Ratio	15.9

The X-ray diffraction data were collected on a Saturn70 CCD diffractometer at 90 K with Mo  $K\alpha$ -radiation for a red needle-shaped crystal with a dimension of 0.25×0.07×0.05 mm<sup>3</sup>. Total 29047 reflections were collected up to 65.4° in 2 $\theta$ , but only 14270 unique reflections with 2 $\theta$  less than 50.0° were used for structure determination. Absorption correction was made by multi-scan method. The structure was solved by direct method with SIR92 and refined by full-matrix least-squares with SHELX97. The difference Fourier map with an initial model consisting of  $\Delta$ - $\Lambda\Lambda\Delta$ / $\Lambda$ - $\Delta\Delta\Lambda$  complex showed positive peaks in the vicinity of the acac ligands that coordinated to Ru(4). These peaks were assigned to carbon atoms of the minor component,  $\Delta$ - $\Lambda\Lambda\Delta$ / $\Lambda$ - $\Delta\Delta\Lambda$  isomer and refined with geometrical restrain. The population ratio was fixed to 3:1 so that the isotropic temperature factors are almost the same for each corresponding atom pair. The crystal has rather large voids, in which several peaks were found on the difference Fourier maps. Some the peaks, which had significant electron density ( $>1.5 \text{ e}\text{\AA}^{-3}$ ), were assigned as oxygen atoms in water molecules that were included as solvent of crystallization and refined with isotropic temperature factors. The H-atoms were included in the calculated positions but no H-atoms in the water molecules were included. The final refinement gave  $wR_2 = 0.2375$ ,  $R_1 = 0.1175$ ,  $S = 1.053$  for 14270 reflections (Two observed reflections with high  $F_c$  values at low 2 $\theta$  were excluded). The largest positive and negative peaks in the difference map were 1.35 and -1.04  $\text{e}\text{\AA}^{-3}$ , respectively. All the computation and graphic drawing were carried out with WinGX package.

**Scheme S1.** Scheme for the calculation of the  $\Delta\epsilon$ 's of enantiomers in fractions (2) and (3).

	(1)	(2)	(3)	(4)
P1	 $3 \Delta\epsilon(\text{hetero})$	 $2\Delta\epsilon(\text{hetero}) - \Delta\epsilon(\text{homo})$	 $-\Delta\epsilon(\text{hetero}) + 2\Delta\epsilon(\text{homo})$	 $3\Delta\epsilon(\text{homo})$
P2	 $-3 \Delta\epsilon(\text{hetero})$	 $-2\Delta\epsilon(\text{hetero}) + \Delta\epsilon(\text{homo})$	 $\Delta\epsilon(\text{hetero}) - 2\Delta\epsilon(\text{homo})$	 $-3\Delta\epsilon(\text{homo})$

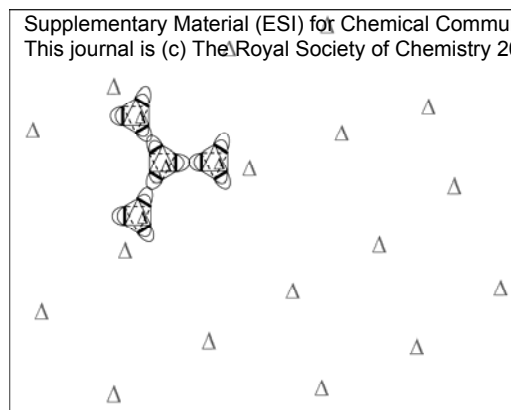
The fractional  $\Delta\epsilon$ 's due to the homo-chiral ( $\Delta$ - $\Delta$  or  $\Lambda$ - $\Lambda$ ) and hetero-chiral ( $\Delta$ - $\Lambda$ ) combinations between the central and peripheral parts (denoted by  $\Delta\epsilon(\text{homo})$  and  $\Delta\epsilon(\text{hetero})$ , respectively). For calculating the  $\Delta\epsilon$ 's of the enantiomers in fractions (2) and (3),  $\Delta\epsilon(\text{homo})$  and  $\Delta\epsilon(\text{hetero})$  were taken to be one-third of  $\Delta\epsilon$ 's of fractions (4) and (1), respectively.



(a) (2)  $\Delta$ - $\Lambda\Lambda\Lambda/\Lambda$ - $\Delta\Delta\Delta$

(b) (3)  $\Delta$ - $\Delta\Delta\Lambda/\Lambda$ - $\Lambda\Lambda\Lambda$

**Figure S3.** The calculated  $\Delta\epsilon$ 's of the enantiomers of fraction (2) (left) and fraction (3) (right) on the basis of Table S2. P1 and P2 denote the less and more retained enantiomers of fractions (2) or (3) on the chiral HPLC column, respectively.



**Figure S4** A schematic drawing of the adsorption of a tetranuclear complex on the surface of the modified clay. The letter,  $\Delta$ , indicates an immobilized  $\Delta$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup> ion. These ions are assumed to form a two-dimensional lattice with their C<sub>3</sub> axes perpendicular to the surface. According to the molecular model,  $\Delta$ -[Ru(acac)<sub>3</sub>] is preferred to its antipode when [Ru(acac)<sub>3</sub>] is placed onto  $\Delta$ -[Ru(II)(phen)<sub>3</sub>]<sup>2+</sup>, while  $\Lambda$ -[Ru(acac)<sub>3</sub>] is preferred to its antipode when [Ru(acac)<sub>3</sub>] is placed between  $\Delta$ -[Ru(II)(phen)<sub>3</sub>]<sup>2+</sup>