Supplementary Information

for

Stereoselective Interactions as Manifested by Vibrational Circular Dichroism Spectra: Interplay between Chiral Metal Complexes Co-adsorbed in a Montmorillonite Clay

Hisako Sato, ^{a*} Kazuyoshi Takimoto, ^a Hirotoshi Mori^b and Akihiko Yamagishi ^c

^aDepartment of Chemistry, Graduate School of Science and Engineering, Ehime University, Matsuyama 790-8577, Japan, <u>sato.hisako.my@ehime-u.ac.jp</u>

^bFaculty of Science, Department of Chemistry, Ochanomizu University, Tokyo 112-8610, Japan

°School of Medicine, Toho University, Ota-ku, Tokyo 143-8540, Japan

Contnets

- 1. Chromatograms for optical resolution of [M(acac)₃]
- 2. X-Ray diffraction measurements of ion-exchange adducts of sodium montmorillonite with [Ru(phen)₃]²⁺ and [Co(acac)₃]
- 3. Experimental VCD and IR spectra of [Co(acac)₃] and [Cr(acac)₃] in CDCl₃
- 4. Experimental VCD and IR spectra of [Ru(phen)₃]²⁺/montmorillonite
- 5. Calculated optimized structures of the associates between Δ -[Ru(phen)₃]²⁺ and Δ or Λ -[Co(acac)₃]
- 6. Calculated optimized structures of the associates between Δ -[Ru(phen)₃]^{2*} and Δ or Λ -[Cr(acac)₃]

1. Chromatograms for optical resolution of [M(acac)₃]

A racemic mixture of $[M(acac)_3]$ (M = Co and Cr) was eluted with methanol on a column packed with an ion-exchange adduct of synthetic hectorite and Δ - $[Ru(phen)_3]^{2+}$. The chromatograms were shown below:



Figure S1. The chromatograms for eluting the racemic mixtures of $[Co(acac)_3]$ (left) and $[Cr(acac)_3]$ (right) with methanol on a chiral column (4 mm (i.d.) x 25 cm; RU-1 (Shiseido Inc. Co. (Japan)), respectively. A flow rate was 1 mLmin⁻¹. Elution was monitored at 250 nm. The dead time of the column was estimated to be 5.73 minutes on eluting chloroform at 295 K. The enantiomeric difference of free energy of adsorption (- ΔG_{ads}) are calculated as below:

[M(acac) ₃]	ratio of elution time	free energy difference of adsorption	
		$-\Delta G_{ads} (\Delta) + \Delta G_{ads} (\Lambda) (kJmole^{-1})$	
[Co(acac) ₃]	Δ/Λ 2.27	2.05	
[Cr(acac) ₃]	Δ/Λ 2.68	2.47	



2. X-Ray diffraction measurements of ion-exchange adducts of sodium montmorillonite with [Ru(phen)₃]²⁺ and [Co(acac)₃]

Diffraction angle (degree)

diffraction patterns of the ion-exchange adducts of Δ -Figure S2. The X-ray $[Ru(phen)_3]^{2+}/montmorillonite (upper), \Delta - [Co(acac)_3]/\Delta - [Ru(phen)_3]^{2+}/montmorillonite (middle)$ and Λ -[Co(acac)₃]/ Δ -[Ru(phen)₃]²⁺/montmorillonite (bottom), respectively. The X-ray wavelength distance determined was 0.1542 nm. The interlayer was to be 1.75 (Δnm $[Ru(phen)_3]^{2+}/montmorillonite)$, 1.78 nm (Δ - $[Co(acac)_3]/\Delta$ - $[Ru(phen)_3]^{2+}/montmorillonite)$ and 1.81 nm $(\Lambda - [Co(acac)_3]/\Delta - [Ru(phen)_3]^{2+}/montmorillonite)$ from the peaks at the smallest diffraction angle, respectively.



3. Experimental VCD and IR spectra of [Co(acac)₃] and [Cr(acac)₃] in CDCl₃

Figure S3. Experimental VCD (upper) and IR (lower) spectra of $[Co(acac)_3]$ (left) and $[Cr(acac)_3]$ (right) in CDCl₃ (modified from H. Sato et al. *Inorg. Chem.* 46, 6755-6766 (2007)). Black and red lines are for the Λ - and Δ -enantiomers, respectively.



4. Experimental VCD and IR spectra of [Ru(phen)₃]²⁺/montmorillonite

Figure S4. Experimental VCD (upper) and IR (lower) spectra of $[Ru(phen)_3]^{2+}$ /montmorillonite: black and red lines are for the Λ - and Δ -enantiomers, respectively (modified from H. Sato et al., *Phys. Chem. Chem. Phys.*, 20, 3141-3147 (2018)).

5. Calculated optimized structures of the associates between Δ -[Ru(phen)₃] and Δ - or Λ -[Co(acac)₃]



Figure. S5. The optimized structures of the molecular associates between Δ -[Ru(phen)₃]²⁺ and Δ -[Co(acac)₃] (left) and between Δ -[Ru(phen)₃] and Λ -[Co(acac)₃] (right).

6. Calculated optimized structures of the associates between Δ -[Ru(phen)₃] and Δ -or Λ -[Cr(acac)₃]



Figure S6. The optimized structures of the molecular associates between Δ - [Ru(phen)₃]²⁺ and Δ -[Cr(acac)₃] (left) and between Δ - [Ru(phen)₃] and Λ -[Cr(acac)₃] (right).