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Two-Step Chiral Transfer from D-Penicillamine to Metallosupramolecular Ionic Crystals

Yuhei Yasukawa, Nobuto Yoshinari, and Takumi Konno*

Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043 (Japan)

konno@chem.sci.osaka-u.ac.jp

Experimental Section

1. Materials.

The racemic complex $(\Delta)_4/(\Lambda)_4$-$[Zn_4O\{Rh(aet)_3\}_4](NO_3)_6\cdot 6H_2O$ ($(\Delta)_4/(\Lambda)_4$-[**1**]$(NO_3)_6\cdot 6H_2O$) was prepared from Δ/Λ-$[Rh(aet)_3]$ by the method of the literature.[16] The optically active complex $(\Delta)_4$-$[Zn_4O\{Rh(aet)_3\}_4](NO_3)_6\cdot 6H_2O$ was prepared by a similar procedure for $(\Delta)_4/(\Lambda)_4$-[**1**]$(NO_3)_6\cdot 6H_2O$ using Δ-$[Rh(aet)_3]$ [23] instead of Δ/Λ-$[Rh(aet)_3]$. Other reagents were of the commercial grade and were used without further purification.

2. Preparation of Complexes.

a) Preparation of $\{(\Lambda)_4$-$[Zn_4O\{Rh(aet)_3\}_4]\}\{\Lambda_D$-$[Rh(D\text{-}pen)_3]\}(NO_3)_3$ (3).

D-Penicillamine (D-H_2pen) (290 mg, 2.0 mmol) was added to a yellow solution containing $(\Delta)_4/(\Lambda)_4$-[**1**]$(NO_3)_6\cdot 6H_2O$ (200 mg, 0.096 mmol) in degassed H_2O (10 mL), which gave a yellow solution (pH 5). Approximately 160 μL of 1 M aqueous NaOH was added to the solution until pH 7 was reached, and the solution was refluxed at 120°C for 2 h under N_2 atmosphere, during which time a yellow precipitate gradually appeared. The resulting yellow suspension was rested at room temperature overnight and then filtered. The collected yellow powder (**3**) was washed with a small amount of cold water, while the orange-yellow filtrate was used for column separation. Yield: 87 mg (41% based on Rh). Anal. Found: C, 17.10; H, 5.11; N, 9.13%. Calcd for $[Zn_4O\{Rh(aet)_3\}_4][Rh(D\text{-}pen)_3](NO_3)_3\cdot 23H_2O$ = $C_{39}H_{145}N_{18}O_{39}Rh_5S_{15}Zn_4$: C, 17.05; H, 5.32; N, 9.18%. IR spectrum (cm^{-1}, KBr disk): 1584 (ν_{COO^-}), 1384 (ν_{NO3^-}). ^{1}H NMR spectrum (δ, ppm from DSS, D_2O): 3.30 (m, 12H), 3.02 (d, J = 13.5 Hz, 3H), 2.78 (m, 24H), 2.59 (m, 12H), 1.50 (s, 9H), 1.21 (s, 9H).

Yellow block crystals of **3** suitable for single-crystal X-ray analysis were obtained by a similar reaction under diluted conditions.

b) Preparation of $\{(\Delta)_4$-$[Zn_4O\{Rh(aet)_3\}_4]\}\{\Lambda_D$-$[Rh(D\text{-}pen)_3]\}(NO_3)_3$ (4).

A yellow aqueous solution containing **3** (30 mg, 11 μmol) was poured onto an SP-Sephadex C-25 (Na^+) column and then treated with water. A pale yellow eluate containing Λ_D-$[Rh(D\text{-}pen)_3]^{3-}$ (Λ_D-[**2**]$^{3-}$) was collected and evaporated to ca. 20 mL. Then, $(\Delta)_4$-[**1**]$(NO_3)_6\cdot 6H_2O$ (24 mg, 12 μmol) was added to this solution. When the resulting pale yellow solution was rest at room temperature for 12 days, yellow block crystals (**4**) suitable for X-ray analysis formed. The crystals were collected by filtration and washed with cold water. Yield: 11 mg (35%

based on Rh). IR spectrum (cm^{-1}, KBr disk): 1584 (ν_{COO^-}), 1384 (ν_{NO3^-}). ^1H NMR spectrum (δ, ppm from DSS, D_2O): 3.30 (m, 15H), 3.02 (d, J = 11.0 Hz, 3H), 2.77 (m, 30H), 2.59 (m, 15H), 1.50 (s, 9H), 1.22 (s, 9H).

3. Physical Measurements.

The absorption spectra were measured with a JASCO V-660 UV/VIS spectrometer at room temperature. The circular dichroism (CD) spectra were measured with a JASCO J-820 spectropolarimeter at room temperature. The IR spectra were recorded with a JASCO FT/IR-4100 infrared spectrometer using KBr disks at room temperature. Elemental analyses (C, H, N) were performed at Osaka University using a Yanaco CHN Corder MT-5. The X-ray fluorescence analyses were conducted using a SHIMADZU Rayny EDX-720 spectrometer. The ^1H NMR spectra were recorded with a JEOL ECAMX-500SP spectrometer in D_2O. Sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as the internal reference. All measurements were performed at the probe temperature. Powder X-ray diffraction patterns were recorded at room temperature in transmission mode [synchrotron radiation λ = 0.999115(18) Å; 2θ range = 0–78°; step width = 0.01°; data collection time = 3 min] on a diffractometer equipped with a white imaging plate detector at the SPring-8 BL02B2 beamline. The samples were rotated during the measurements. The diffraction patterns were collected with a large Debye-Scherrer camera. The powder simulation patterns were generated from the single-crystal X-ray structures using Mercury 3.5.

4. X-ray Structural Determinations.

Single-crystal X-ray diffraction data for **3** were recorded on an ADSC Q210 CCD area detector with a synchrotron radiation (λ = 0.6000 Å) at 2D beamline in Pohang Accelerator Laboratory (PAL). The intensity data were collected by the ω-scan technique and the diffraction images were processed by using HKL3000.[S1] Absorption correction was performed by using HKL3000.[S1] The structure of **3** was solved by direct methods using SHELXS-2014.[S2] The structure refinements were carried out using full-matrix least-squares (SHELXL-2014).[S2] All calculations were performed using the Yadokari-XG software package.[S3] One third of the octanuclear complex cation $(\Lambda)_4$-$[Zn_4O\{Rh(aet)_3\}_4]^{6+}$, one third of the mononuclear complex anion Λ_D-$[Rh(D\text{-}pen)_3]^{3-}$, and one NO_3^- anion, along with solvated water molecules, were crystallographically independent. One of the Λ-$[Rh(aet)_3]$ units and one of aet ligand belonging to another Λ-$[Rh(aet)_3]$ unit in $(\Lambda)_4$-$[Zn_4O\{Rh(aet)_3\}_4]^{6+}$ and two oxygen atoms of carboxylate group in Λ_D-$[Rh(D\text{-}pen)_3]^{3-}$ were disordered. Hydrogen atoms were included in the calculated positions, except those of water molecules. All non-hydrogen

atoms, except water molecules, nitrate anions and the disordered atoms, were anisotropically refined. Several DFIX, SADI, DELU, SIMU and ISOR restraints were used to model the complexes and nitrate anions.

The single-crystal X-ray diffraction measurement for **4** was performed using a Rigaku FR-E Superbright rotating-anode X-ray source with a Mo target (λ = 0.71075 Å), equipped with a Rigaku RAXIS VII imaging plate as a detector, at 100 K. The intensity data were collected via the ω-scan technique and empirically corrected for absorption. The structure of **4** was solved by direct methods using SHELXS2014. The structure refinements were performed using full matrix least-squares (SHELXL2014). The data are summarized in Table S1. One complex cation of $(\Delta)_4$-$[Zn_4O\{Rh(aet)_3\}_4]^{6+}$, one complex anion of Λ_D-$[Rh(D\text{-}pen)_3]^{3-}$, and three NO_3^- anions, along with solvated water molecules, were crystallographically independent. Hydrogen atoms were included in the calculated positions, except those of H_2O molecules. All non-hydrogen atoms, except water molecules and nitrate anions, were anisotropically refined. Several DFIX, DELU, ISOR and FLAT restraints were used to model the complexes and nitrate anions.

Table S1. Crystallographic data of **3** and **4**.

	{(Λ)$_4$-[Zn$_4$O{Rh(aet)$_3$}$_4$]}{Λ$_D$-[Rh(D-pen)$_3$]}(NO$_3$)$_3$·12H$_2$O (**3**)	{(Δ)$_4$-[Zn$_4$O{Rh(aet)$_3$}$_4$]}{Λ$_D$-[Rh(D-pen)$_3$]}(NO$_3$)$_3$·20H$_2$O (**4**)
Formula	$C_{39}H_{123}N_{18}O_{28}Rh_5S_{15}Zn_4$	$C_{39}H_{139}N_{18}O_{36}Rh_5S_{15}Zn_4$
Color, form	Yellow, block	Yellow, block
Mw	2549.48	2693.60
Crystal system	Trigonal	Triclinic
Space group	*R*3	*P*1
a/ Å	20.2090(3)	13.279(9)
b/ Å	20.2090(3)	13.782(10)
c/ Å	21.1201(4)	14.450(10)
α(°)	90	95.771(15)
β (°)	90	94.901(10)
γ (°)	120	96.534(16)
V/ Å^3	7469.9(3)	2602(3)
Z	3	1
T/ K	100(2)	100(2)
ρ calcd / g· cm^{-3}	1.700	1.719
*R*1 (I>2σ(I))[a)]	0.0908	0.0850
w*R*2 (all data) [b)]	0.2922	0.2410
Flack	0.062(10)	0.053(13)

a) $R1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$.

b) $wR2 = [\Sigma(w(F_o^2-F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2}$.

Table S2. The result of mass balance calculation of the Rh^{III} species and their optical purities.

	Rh^{III} species	Rh^{3+} mmol	Optical purity (%)
Starting compound	$(\Delta)_4/(\Lambda)_4$-$[\mathbf{1}]^{6+}$	0.384	0
Products	$[\mathbf{1}]^{6+}$ in crystals **3**	0.127[a]	100 (Λ)
	$[\mathbf{2}]^{3-}$ in crystals **3**	0.032[a]	100 (Λ)
	$[\mathbf{1}]^{6+}$ in the filtrate	0.136[b]	76 (Δ excess)

[a]The values were evaluated based on the yield of **3**. [b]The value was evaluated based on the absorption spectral measurement of the eluate obtained by the column chromatography.

Table S3. Selected intermolecular hydrogen bond distances in **3** and **4**

	3	**4**
$d_{N\cdots O}$/Å (N–H···O–C)	2.85(4), 2.77(4), 2.79(3), 3.02(5), 3.02(4)	2.84(4), 2.89(3), 3.08(4), 2.75(2), 3.20(3), 2.86(3), 2.87(3), 3.06(3), 3.18(3)
$d_{N\cdots S}$/Å (N–H···S)	3.44(5), 3.17(5), 3.00(5)	3.22(3), 3.42(2), 3.56(3)

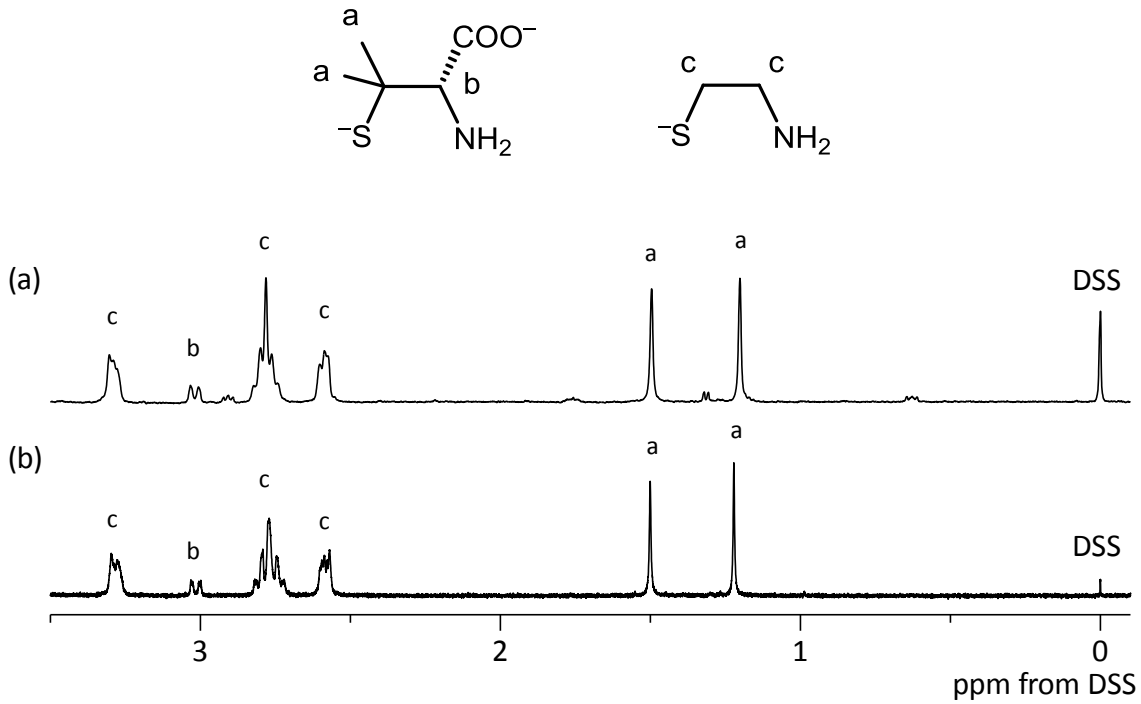

Figure S1. ^{1}H NMR spectra of (a) **3** and (b) **4** in D_2O.

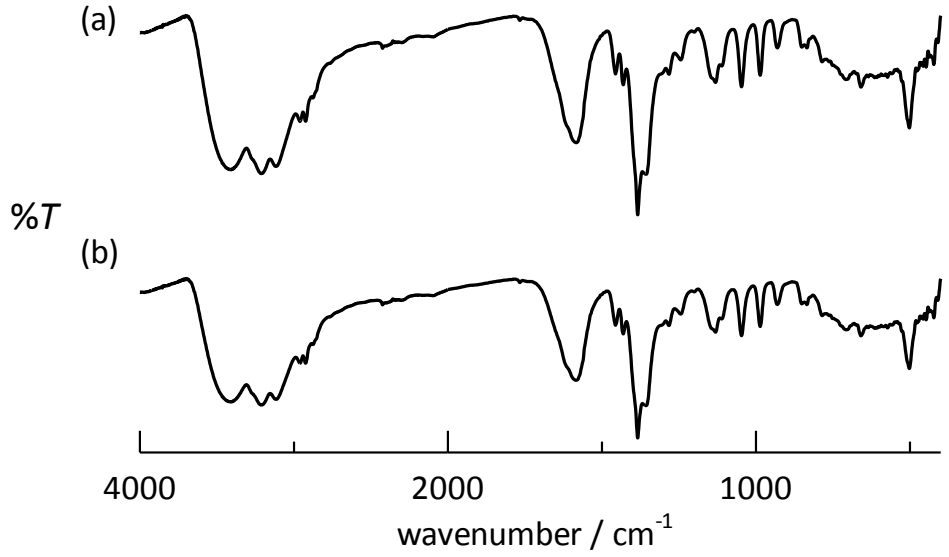

Figure S2. IR spectra of (a) **3** and (b) **4** in KBr pellets.

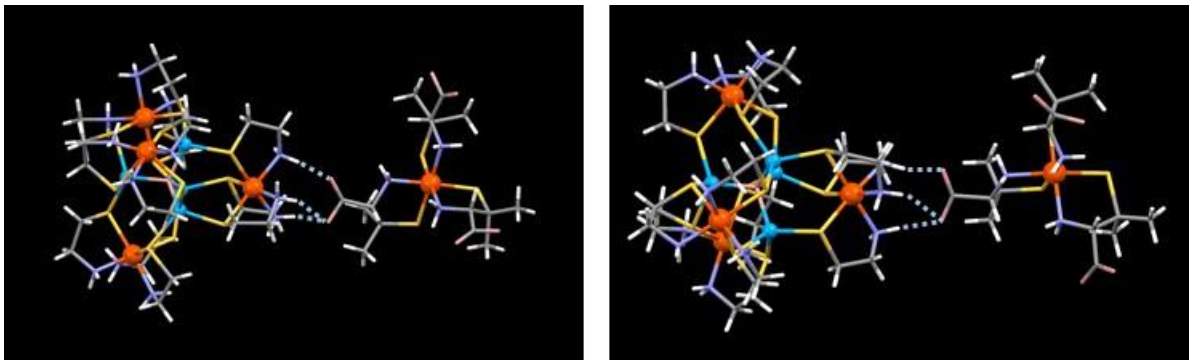

Figure S3. Views of the N–H···O hydrogen bonds (blue dotted lines) between $[\mathbf{1}]^{6+}$ and Λ_D-$[\mathbf{2}]^{3-}$ in (left) **3** and (right) **4**. Each of the three amine groups of $[\mathbf{1}]^{6+}$ forms a hydrogen bond with one of the two carboxylate O atoms of Λ_D-$[\mathbf{2}]^{3-}$. One of the disordered part is selected. Color codes: Rh, orange; Zn, blue; S, yellow; O, pink; N, blue; C, gray, H, white.

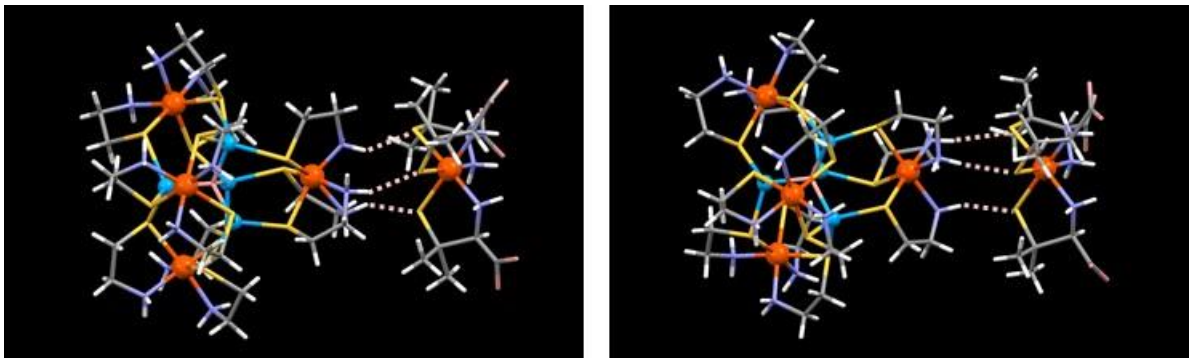

Figure S4. A view of the N–H···S interactions (pink dotted lines) between $[\mathbf{1}]^{6+}$ and Λ_D-$[\mathbf{2}]^{3-}$ in (left) **3** and (right) **4**. One of the disordered part is selected. Each of the three amine groups of $[\mathbf{1}]^{6+}$ forms a hydrogen bond with one of three thiolato S atoms of Λ_D-$[\mathbf{2}]^{3-}$. Color codes: Rh, orange; Zn, blue; S, yellow; O, pink; N, blue; C, gray, H, white.

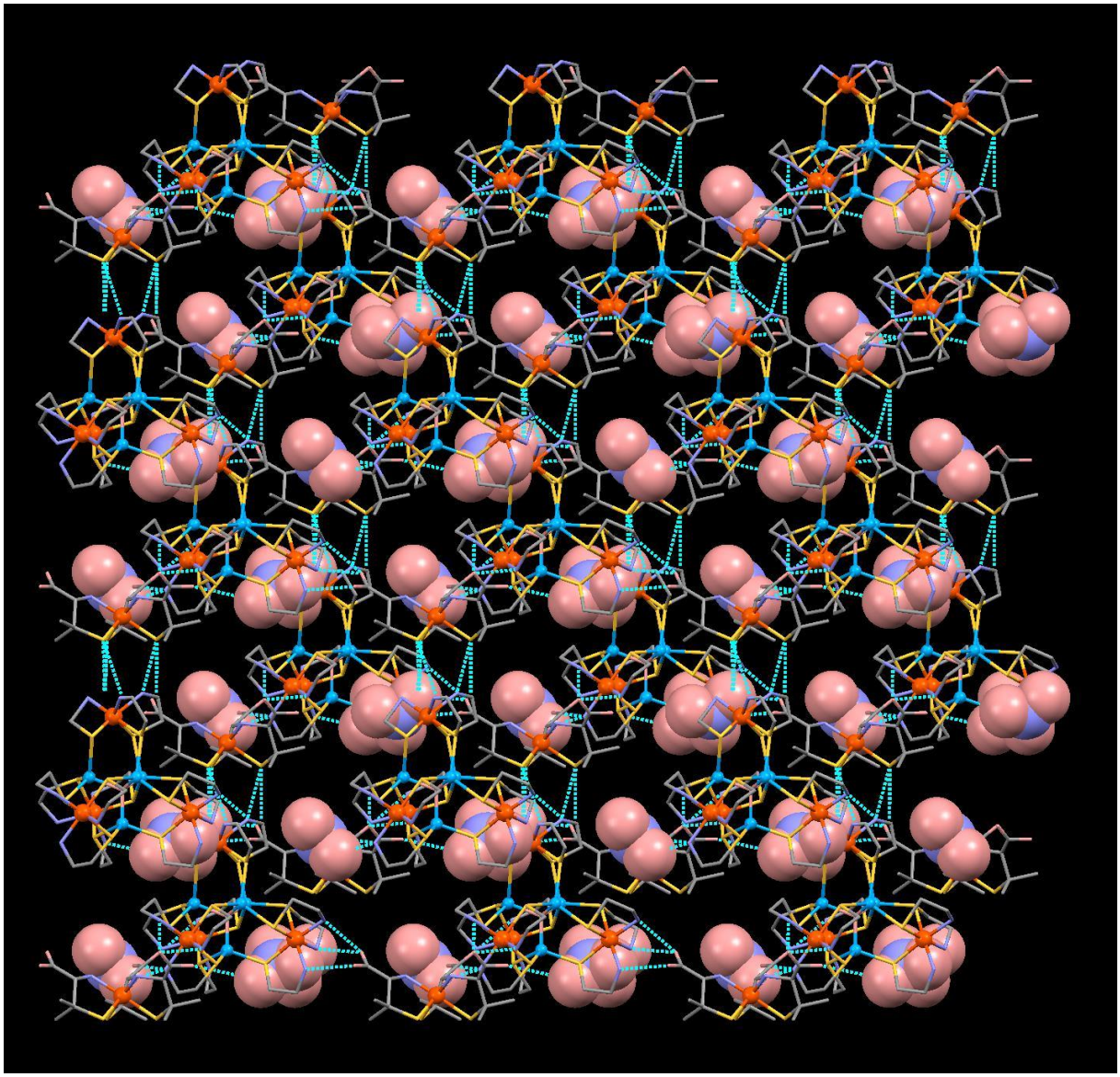

Figure S5. The packing structure of **3**. Dashed lines represent hydrogen bonds. One of the disordered part is selected. Water molecules were omitted for clarity. Color codes: Rh, orange; Zn, blue; S, yellow; O, pink; N, blue; C, gray, H, white.

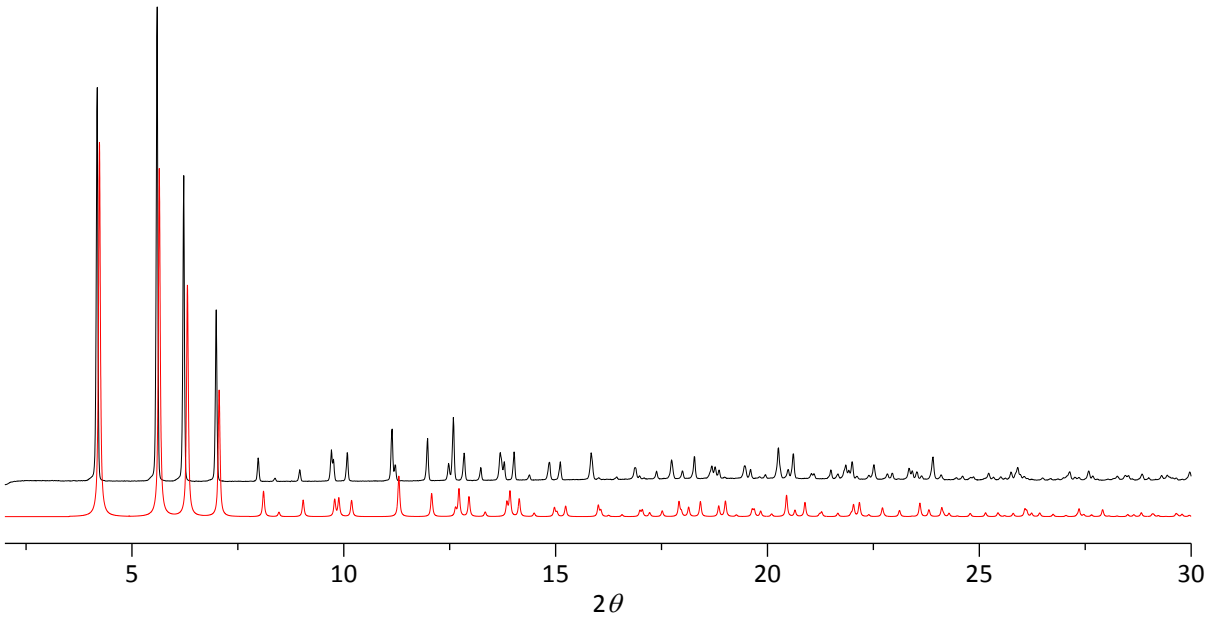

Figure S6. Observed (black) and calculated (red) PXRD patterns of **3**.

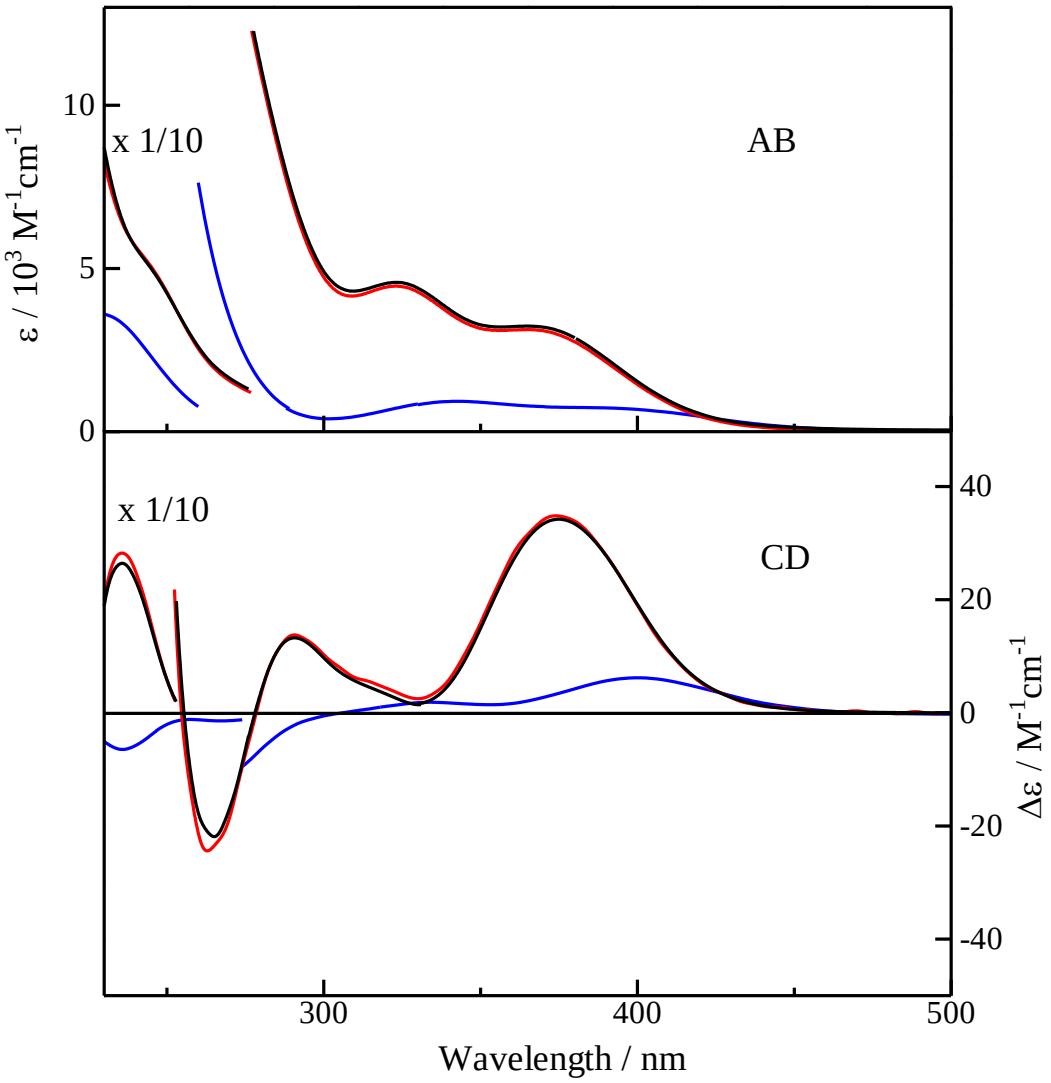

Figure S7. Absorption (AB) and CD spectra of $[\mathbf{1}]^{6+}$ (——) and $[\mathbf{2}]^{3-}$ (——) separated by column chromatography from a solution of **3** and $(\Lambda)_4$-$[\mathbf{1}]^{6+}$ (——) in water.

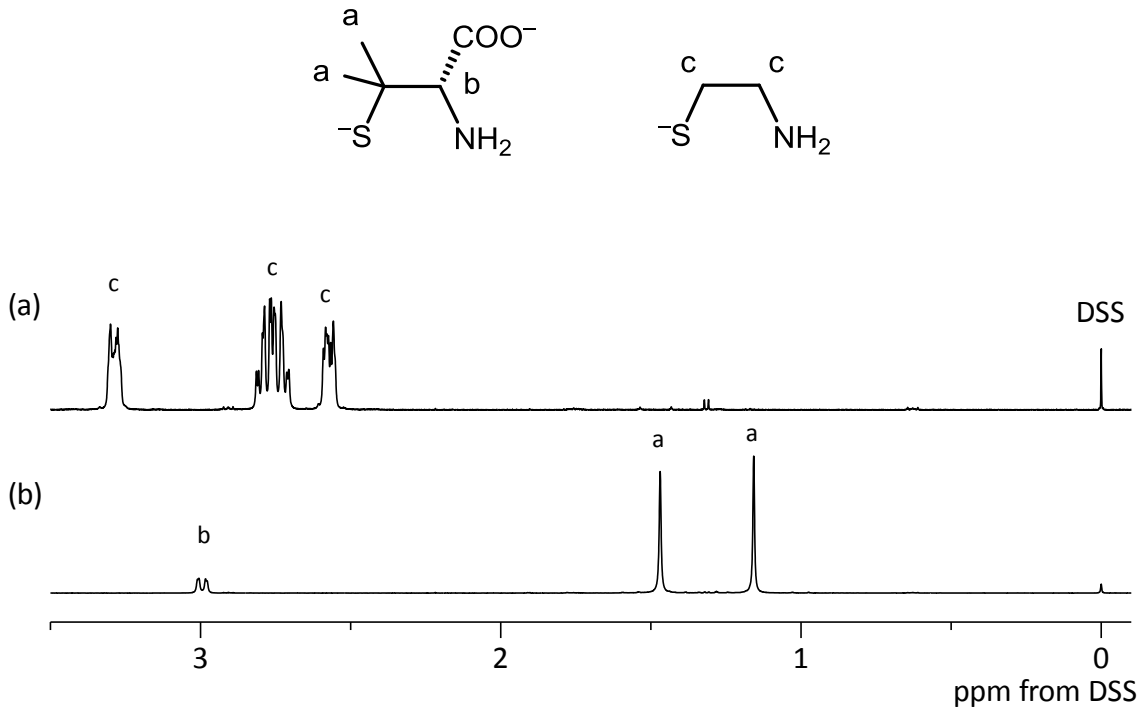

Figure S8. ^{1}H NMR spectra (D_2O) of (a) the cationic species and (b) the anionic species separated by column chromatography from a solution of **3**.

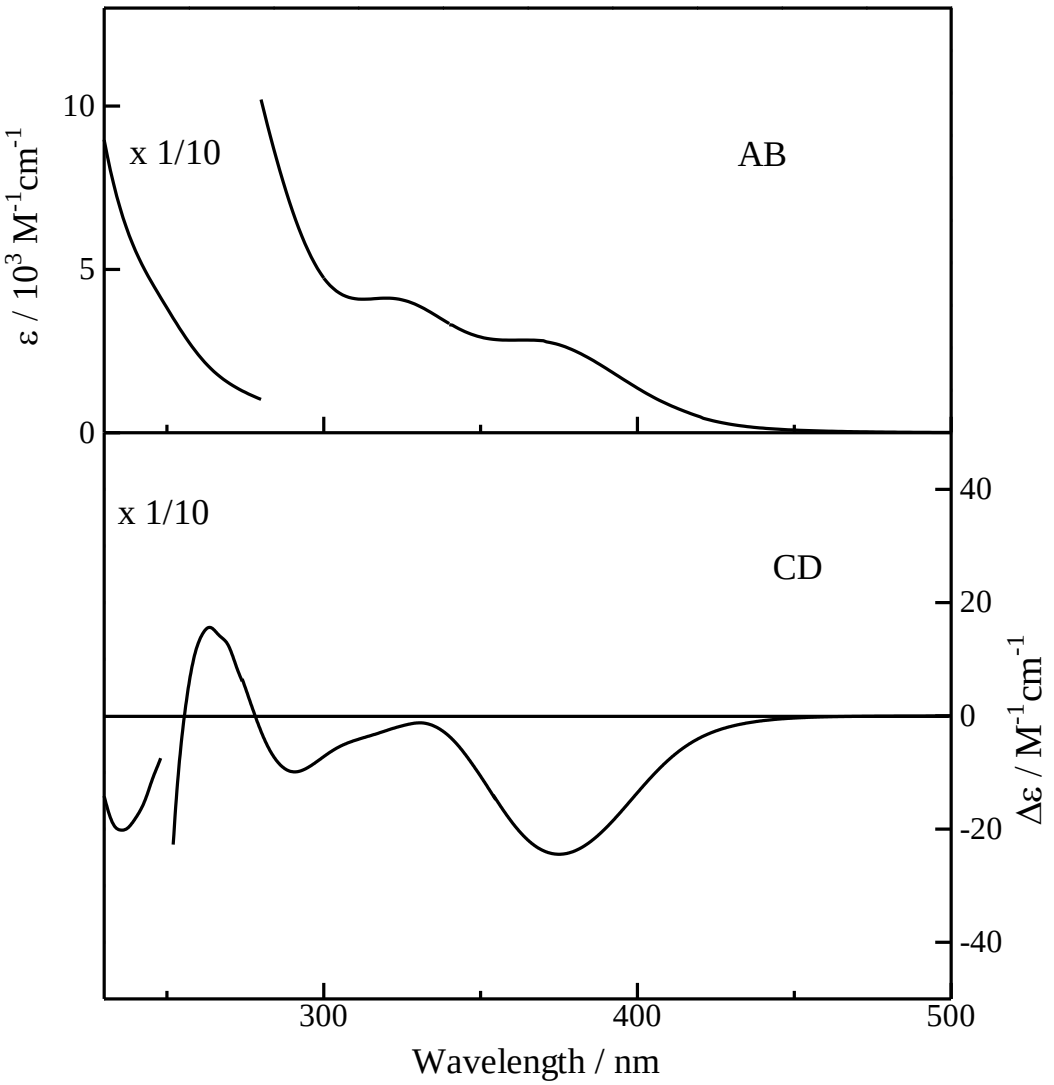

Figure S9. Absorption (AB) and CD spectra of the cationic species separated by column chromatography from the reaction solution after removal of **3**.

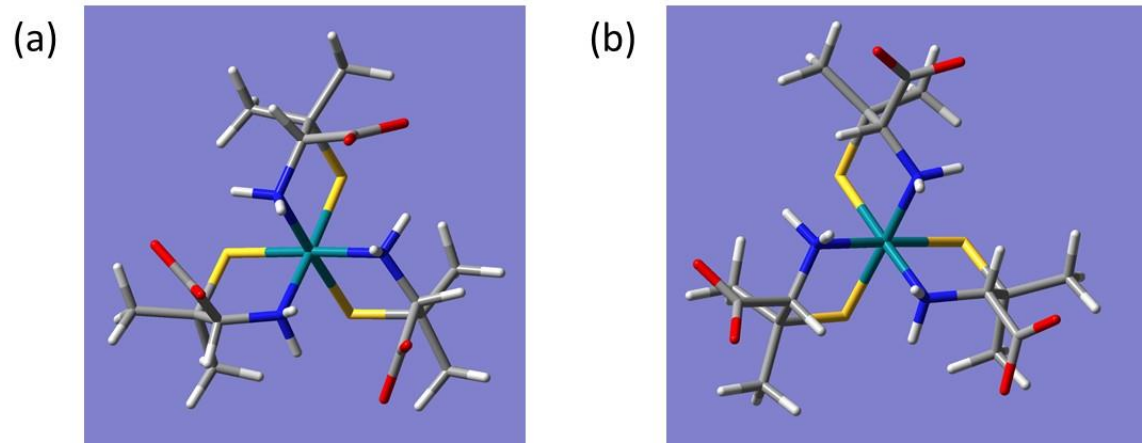

Figure S10. Perspective views of the optimized structures of (a) Δ_D-[Rh(D-pen)$_3$]$^{3-}$ (Δ_D-[**2**]$^{3-}$) and (b) Λ_D-[Rh(D-pen)$_3$]$^{3-}$ (Λ_D-[**2**]$^{3-}$). Rh: blue-green, C: gray, H: white, N: blue, O: red, S: yellow. The optimization calculations were performed with the Gaussian 09 program [S4] at the UFF level.[S5] The total energy of Δ_D-[**2**]$^{3-}$ (274.01 kJ/mol) is much larger than that of Λ_D-[**2**]$^{3-}$ (149.44 kJ/mol), with the much shorter intramolecular distance between COO^- and methyl groups in Δ_D-[**2**]$^{3-}$ (C···O = 2.858 Å) relative to that in Λ_D-[**2**]$^{3-}$ (C···O = 3.064 Å).

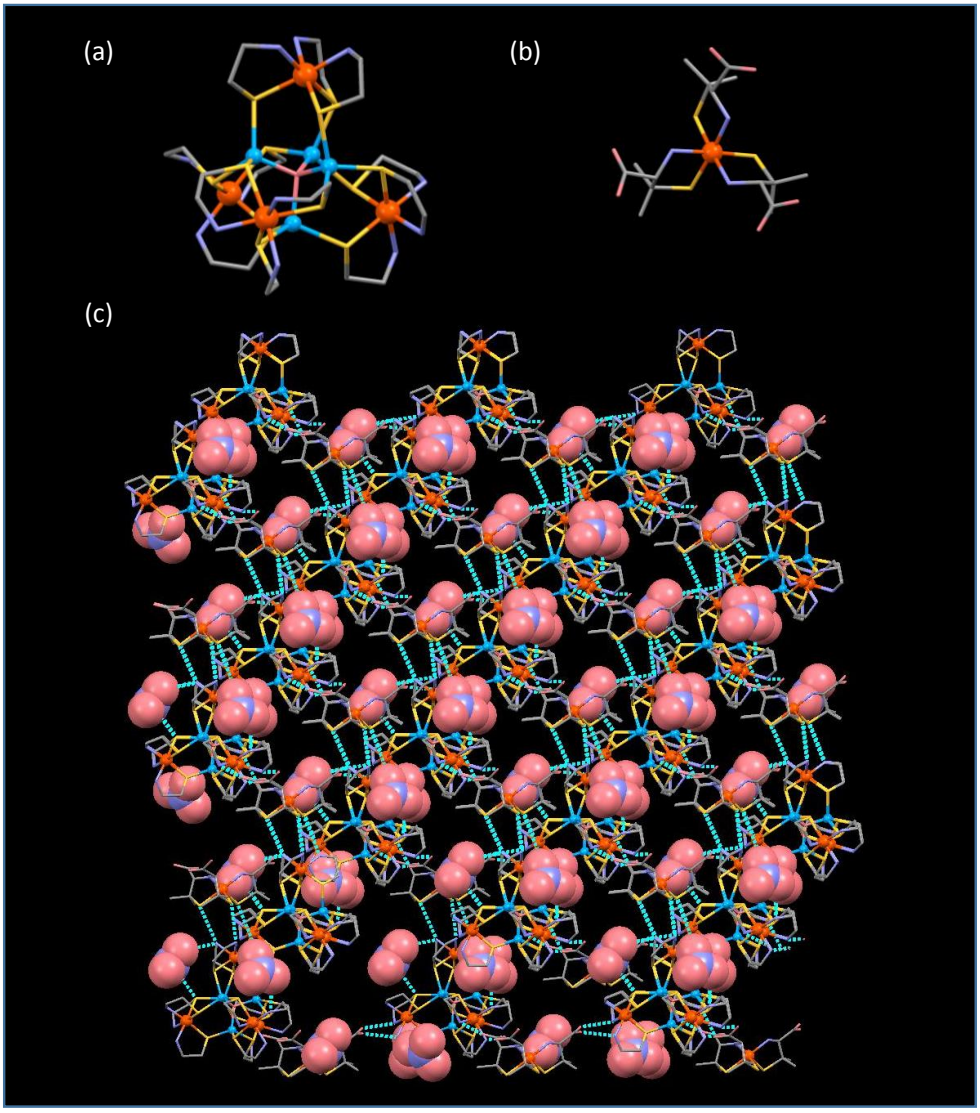

Figure S11. Perspective views of the molecular structures of (a) $(\Delta)_4$-$[Zn_4O\{Rh(aet)_3\}_4]^{6+}$ ($(\Delta)_4$-[**1**]$^{6+}$) and (b) Λ_D-$[Rh(D\text{-pen})_3]^{3-}$ (Λ_D-[**2**]$^{3-}$) and (c) packing structure in **4**. Dashed lines represent hydrogen bonds. Hydrogen atoms and water molecules are omitted for clarity. Color codes: Rh, orange; Zn, blue; S, yellow; O, pink; N, blue; C, gray.

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