Supporting Information

An Unprecedented Up-Field Shift in ^{13}C NMR Spectrum for Carboxyl Carbon of Lantern-Type Dinuclear Complex TBA[$Ru_2(O_2CCH_3)_4Cl_2$] (TBA^+ = Tetra(n-butyl)ammonium Cation)

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Experimental Section

Synthesis of **1**

$Ru_2(O_2CCH_3)_4Cl$ (200 mg, 0.4 mmol) and 0.4mmol TBACl (Tetra(*n*-butyl)ammonium chloride, ca.120mg) were stirred in CH_2Cl_2. After several hours this solution became clear. To this solution added hexane, and then the precipitate was collected by suction. The yield was 290mg (93% based on $Ru_2(O_2CCH_3)_4Cl$). Anal. Calc. for $C_{24}H_{48}Cl_2NO_8Ru_2$: C, 38.35; H, 6.44; N, 1.86. Found: C, 38.31; H, 6.04; N, 2.00. IR(KBr, cm^{-1}) =3541(w), 3461(w), 2961(w), 2875(w), 1437(vs), 1347(w), 688(s)

^1H NMR (500MHz, CD_2Cl_2, 25°C) δ 0.4 (s, 12H, TBA^+), -0.7 (s, 8H, TBA^+), -2.8 (s, 8H, TBA^+), -3.5 (s, 8H, TBA^+), -42.6 (s, 12H, CH_3).
^{13}C NMR (125MHz, CD_2Cl_2, 25°C) δ 56.9 (t, J= 144Hz, TBA^+), 20.0 (t, J=131Hz, TBA^+), 17.5 (t, J=126Hz, TBA^+), 12.4 (q, J=126Hz, TBA^+), -140 (q, J=126Hz, CH_3), -763 (s, CO_2).

Evaluation of contact shift ($\delta_{contact}$)

The $\delta_{contact}$ values were evaluated by using the following equation (see ref. 22):

$$\delta_{contact} = m(S+1)\rho_{\alpha\beta}/T$$

where S (=3/2) is the spin state, $\rho_{\alpha\beta}$ is Fermi contact spin density at the nucleus of interest (DFT calculation of **1** afforded $\rho_{\alpha\beta}$(in au) = -4.715×10^{-3} (per carboxyl carbon) and -1.000×10^{-3} (per methyl carbon)), T is the absolute temperature (298.15 K), and m is a collection of physical constants:

$$m = (\mu_0\mu_B^2 g_e^2)/9k = 23.5 \times 10^6 \text{ ppm K au}^{-1}$$

Table S1. Crystal and experimental data for **1**·CH_2Cl_2

Chemical formula : $C_{26}H_{52}Cl_6NO_8Ru_2$

Formula weight = 921.53

T = 90(2)K

Crystal system : triclinic — Space group : $P\bar{1}$

a = 11.9262(14) Å — α = 76.860(2)°

b = 12.4678(15) Å — β = 82.601(2)°

c = 13.3115(16) Å — γ = 86.546(2)°

V = 1910.5(4) Å^3 — Z = 2

D_x = 1.602 g/cm^3

Radition : Mo Kα (λ = 0.71073)

μ (Mo Kα) = 1.252mm^{-1} — F(000) = 938

Crystal size = 0.60 x 0.53 x 0.30 mm^3

No. of reflections collected = 11700

No. of indeoendent reflectinos = 8366

θ range for data collection : 1.58 to 28.31°.

Data / restraints / parameters : 8366 / 0 / 438

Goodness-of-fit on F^2 = 1.074

R indices [I>2σ(I)] : R1 =0.0313, wR2 = 0.0838

R indices (all data) : R1 =0.0368, wR2 = 0.0859

$(\Delta/\sigma)_{max}$ = 0.002

$(\Delta\rho)_{max}$ = 1.084 Å^{-3} — $(\Delta\rho)_{min}$ = -0.611 Å^{-3}

Measurement: Bruker Smart APEX CCD difractometer

Program system: SHELXTL

Structure determination: Direct methods (SHELXS-97)

Refinement: full: full matrix least-squares (SHELXL-97)

CCDC deposition number: 998328

Table S2. Selected bond Distances (Å) and Angles (°) of **1**

Ru1-Ru1A[i)]	2.3019(4)	Ru2-Ru2A [ii)]	2.3006(5)
Ru1-O1	2.0288(17)	Ru2-O5	2.0297(18)
Ru1-O2	2.0293(17)	Ru2-O6	2.0254(19)
Ru1-O3	2.0306(16)	Ru2-O7	2.0322(18)
Ru1-O4	2.0279(1)	Ru2-O8	2.0193(18)
Ru1-Cl1	2.5316(6)	Ru2-Cl2	2.5181(7)
O1-Ru1-O3	88.74(7)	O5-Ru2-O7	89.36(7)
O1-Ru1-O4	90.80(7)	O5-Ru2-O8	90.70(8)
O2-Ru1-O3	90.98(7)	O6-Ru2-O7	90.00(7)
O2-Ru1-O4	89.42(7)	O6-Ru2-O8	89.89(7)
Cl1-Ru1-Ru1A [i)]	176.540(18)	Cl2-Ru2-Ru2A [ii)]	176.55(2)

Symmetry codes : i) 2-x, -y, -z ii) 1-x, 1-y, 1-z

Table S3. Theoretically and experimentally obtained redox potentials for Ru_2^{4+}/Ru_2^{5+} and Ru_2^{5+}/Ru_2^{6+} (V vs. SCE)

Calculation models	$E_{1/2}(Ru_2^{4+} / Ru_2^{5+})$	$E_{1/2}(Ru_2^{5+} / Ru_2^{6+})$
$[Ru_2(O_2CCH_3)_4Cl_2]^-$	-0.32	1.33
$[Ru_2(O_2CCH_3)_4Cl]$	0.06	2.11
$[Ru_2(O_2CCH_3)_4]^+$	0.76	3.14
Experimental[a)]	-0.34	1.33

a) See text.

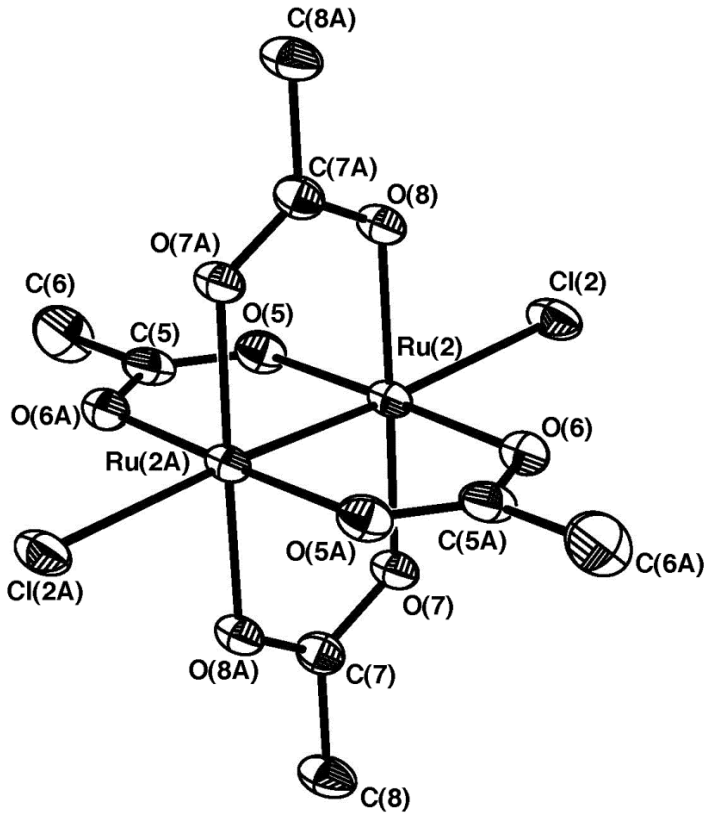

Fig. S1. ORTEP drawing of the Ru2-Ru2A dinuclear unit of **1**•2CH_2Cl_2 showing the thermal ellipsoids at 25% probability level. Hydrogen atoms are omitted for clarity.

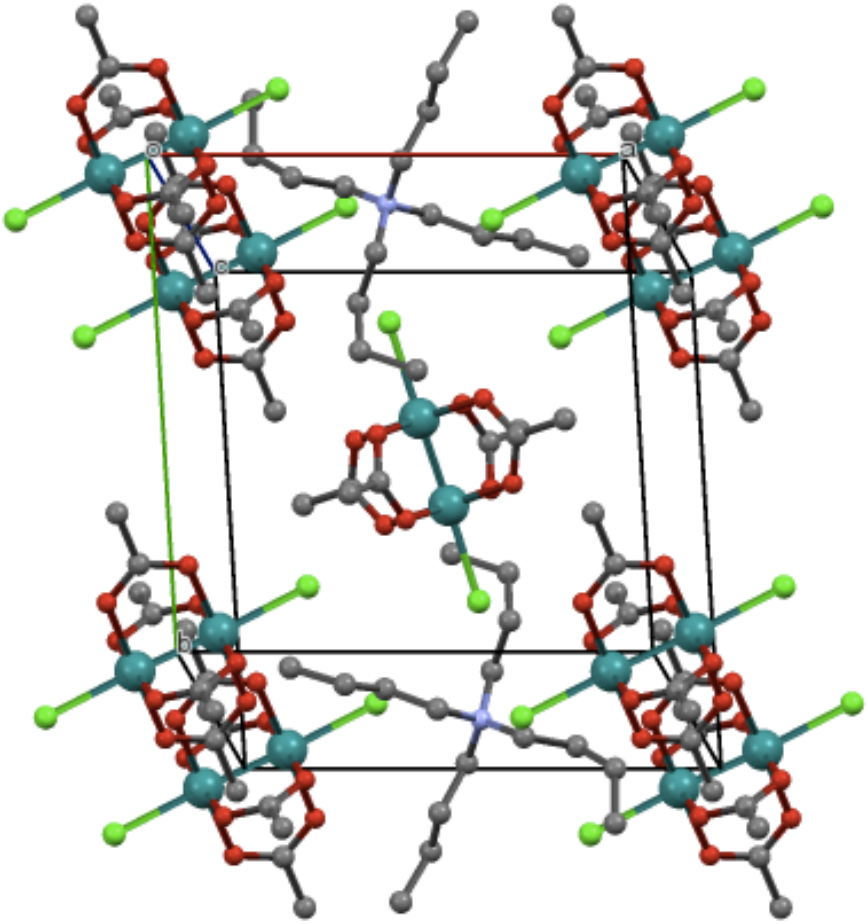

Fig. S2. Packing diagram of **1**. Hydrogen atoms and solvent molecules are omitted for clarity.

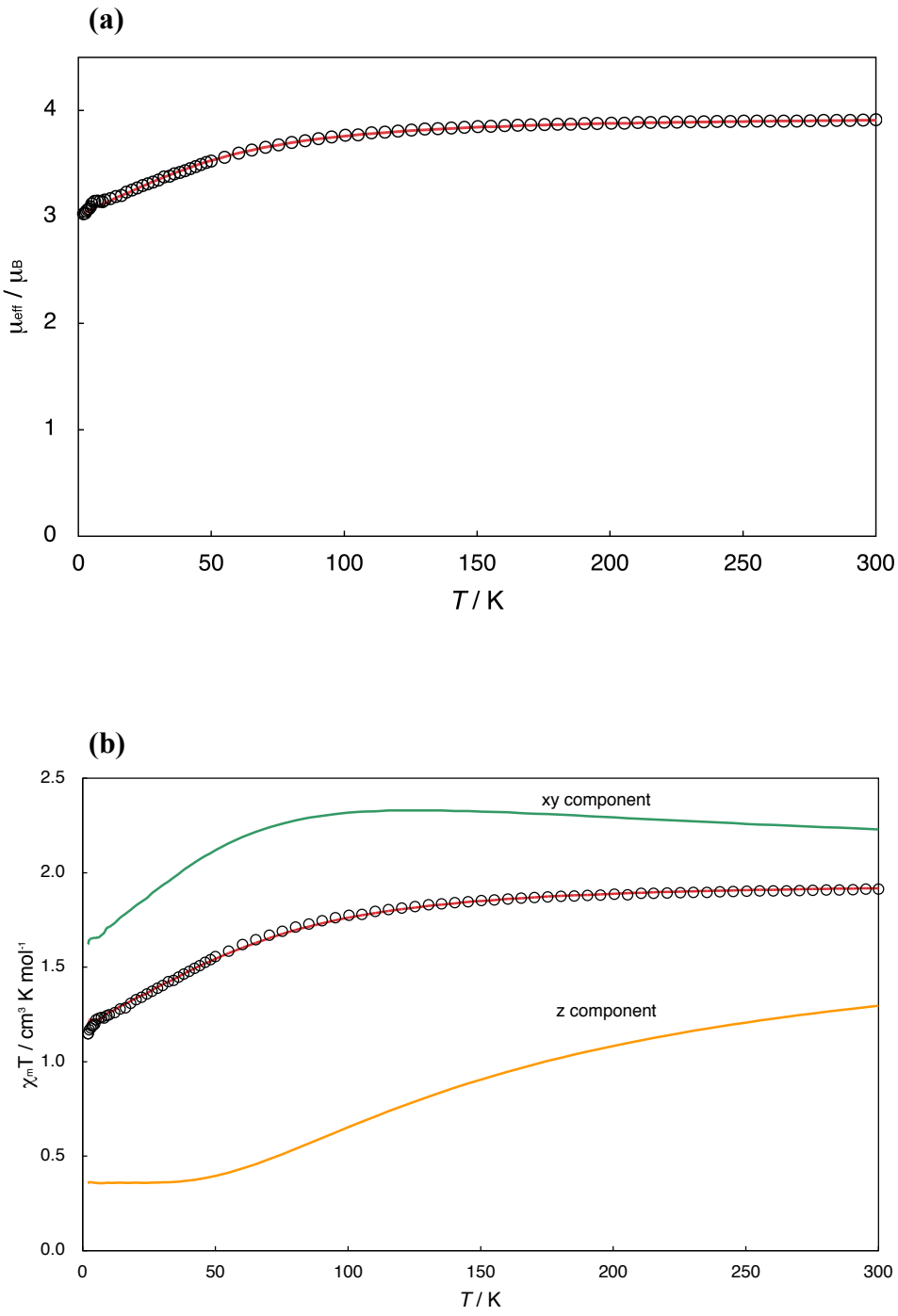

Fig. S3 Plots of μ_{eff} versus T for **1**, red line being drawn with the parameter values described in the text [(**a**) top]. Plots of $\chi_M T$ for **1**, solid lines being drawn with the parameter values described in the text [(**b**) bottom].

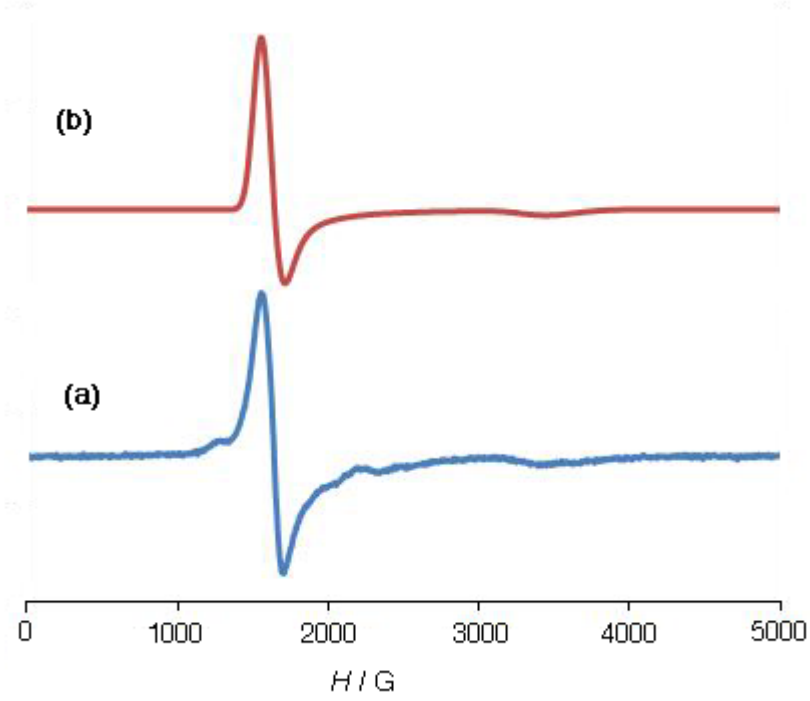

Fig. S4 EPR spectrum of **1** (**a**) in solid at 4K. The simulated spectrum (**b**) is drawn with the parameter values in the text. 1 G = 0.1 mT.

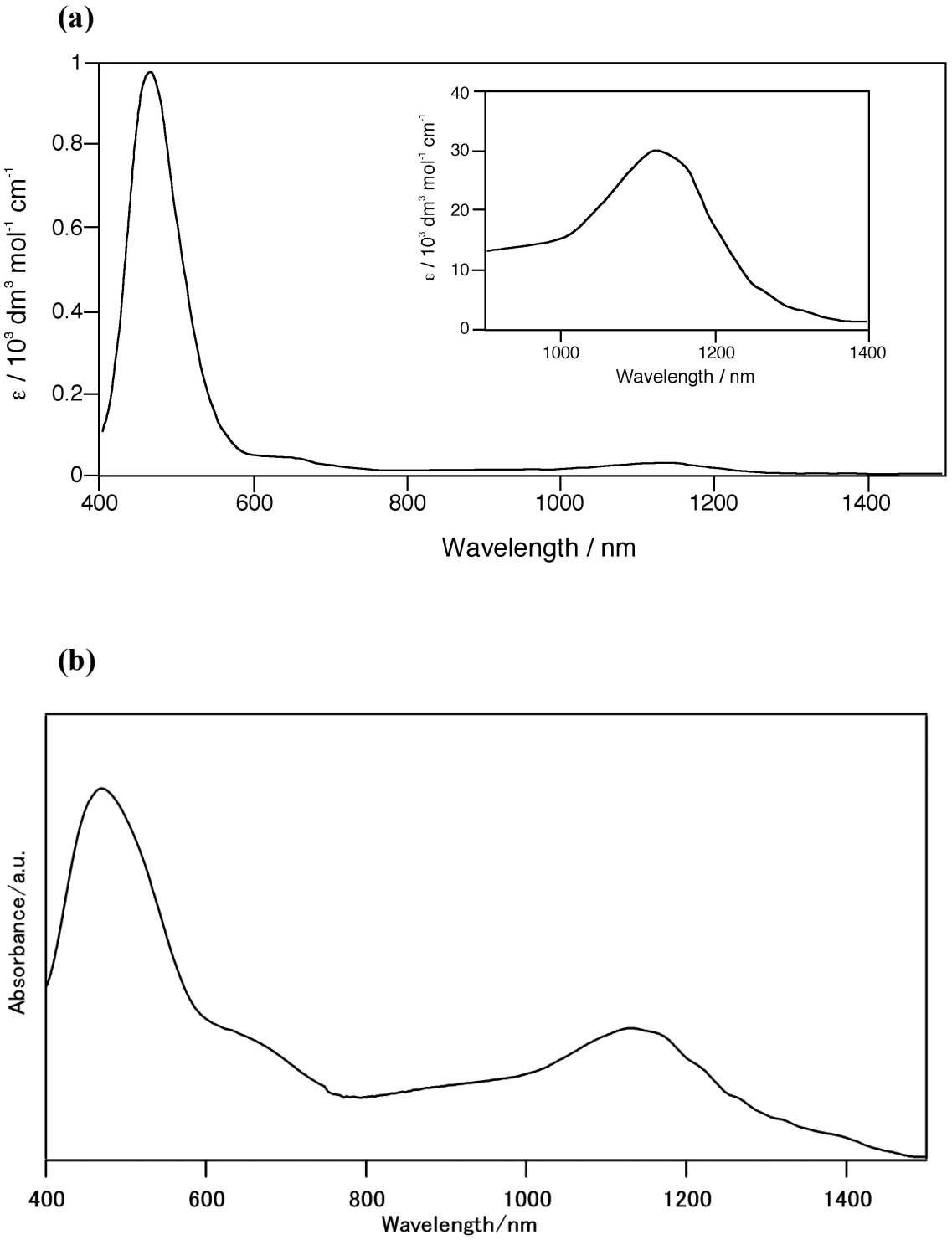

Fig. S5 Absorption spectrum of **1** in CH_2Cl_2 [(**a**) top] and diffuse reflectance spectrum of **1** [(**b**) bottom].

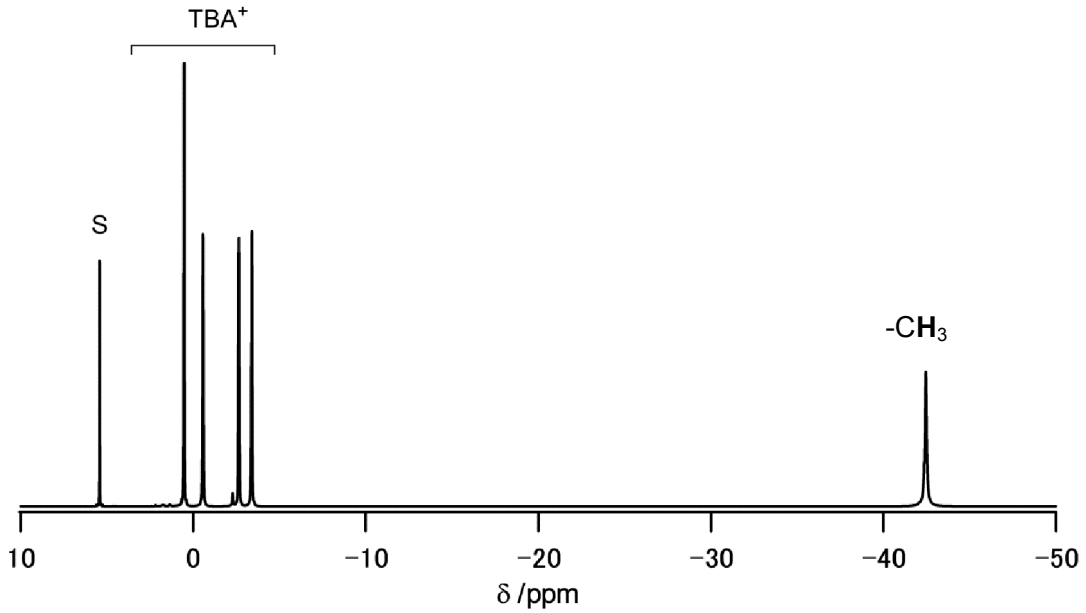

Fig. S6 ^{1}H NMR Spectrum of **1** in CD_2Cl_2 at 25˚C.

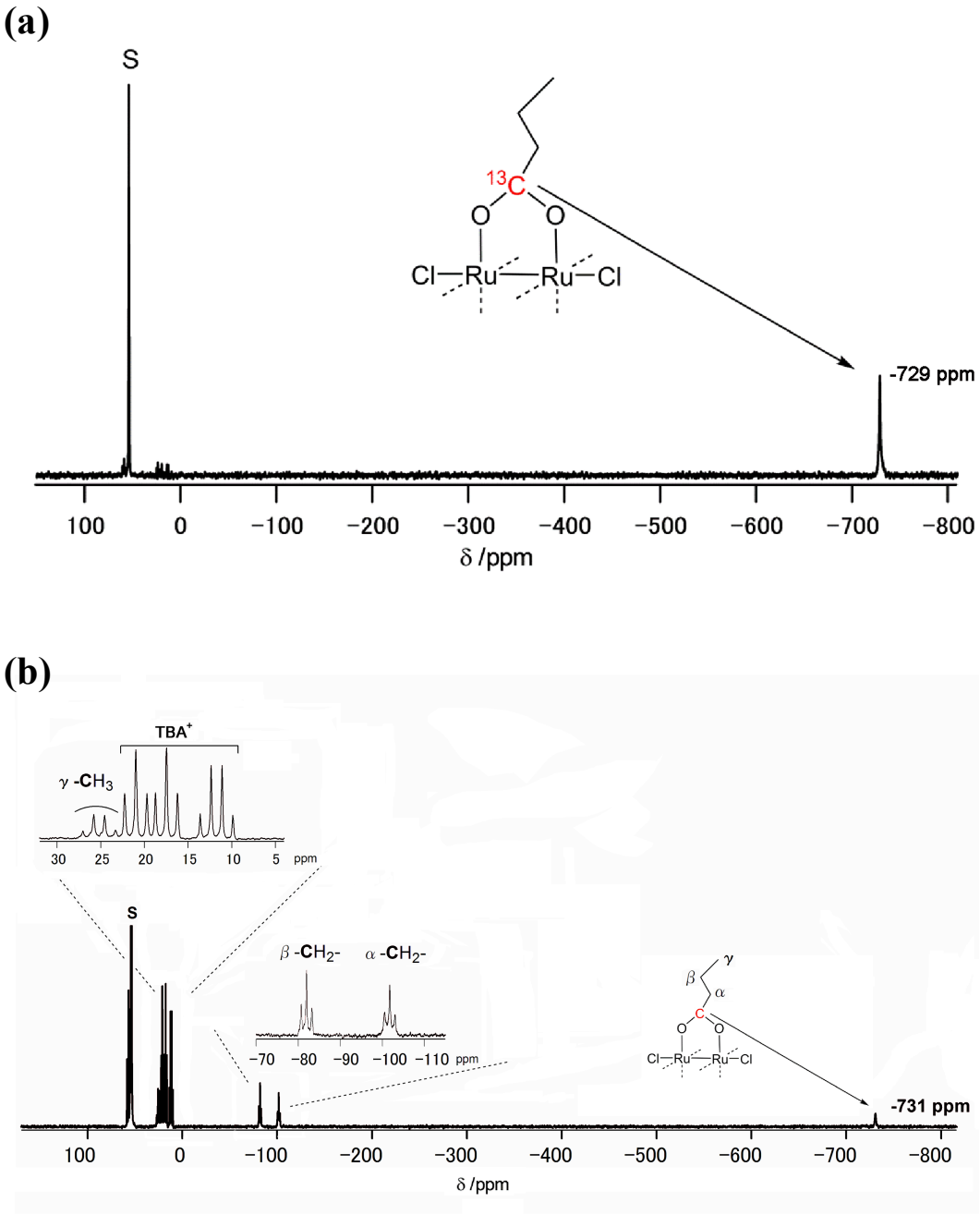

Fig. S7. ^{13}C NMR Spectrum of $[Ru_2\{O_2{}^{13}C(CH_2)_2CH_3\}_4Cl_2]^-$ [(**a**) top] and $[Ru_2\{O_2C(CH_2)_2CH_3\}_4Cl_2]^-$ [(**b**) bottom], which were measured by adding TBA(Cl) to $[Ru_2\{O_2{}^{13}C(CH_2)_2CH_3\}_4Cl]$ or $[Ru_2\{O_2C(CH_2)_2CH_3\}_4Cl]$ in CD_2Cl_2 at 25°C.

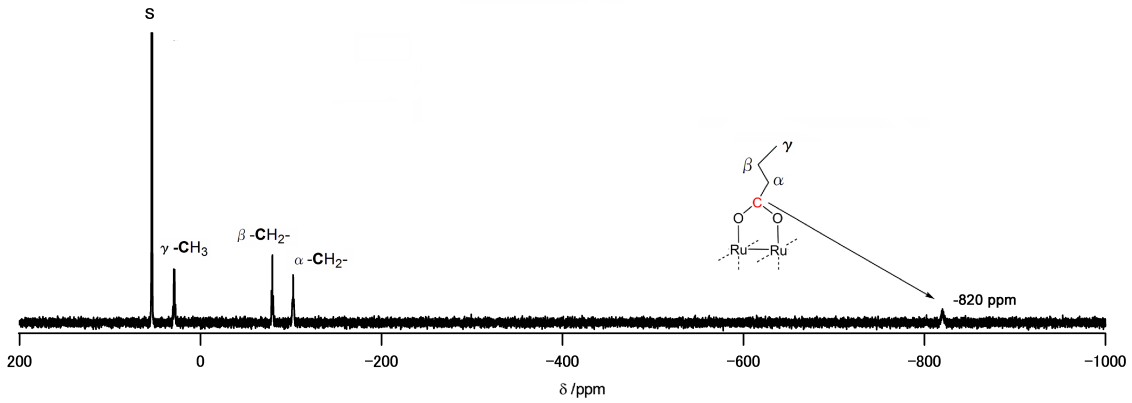

Fig. S8. ^{13}C NMR Spectrum of $[Ru_2\{O_2C(CH_2)_2CH_3\}_4]BF_4$, which was measured in CD_2Cl_2 at 25˚C.

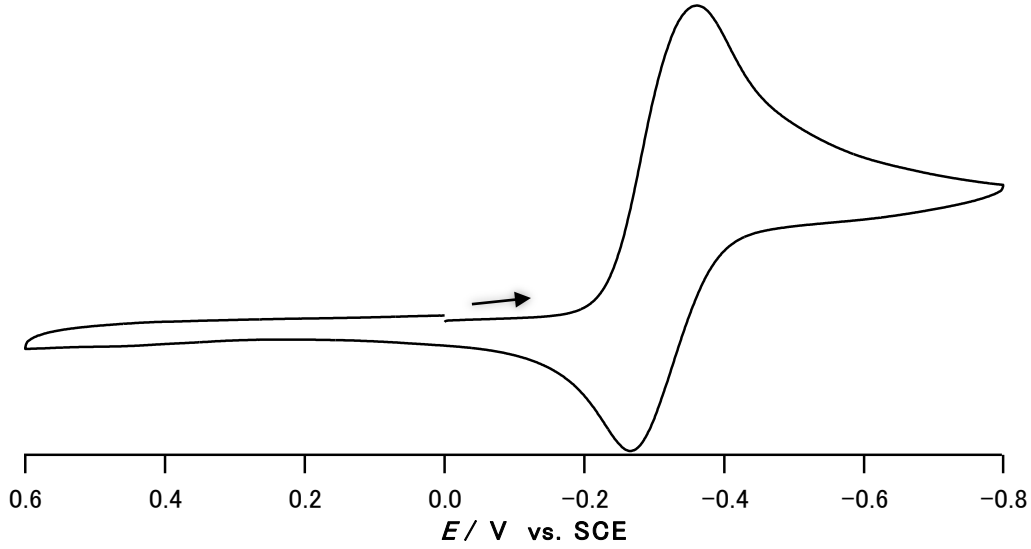

Fig. S9. Cyclic voltammogram(CV) of complex **1** in dichloromethane; scan rate = 50 mV s^{-1}, [complex] = 1x 10^{-3} M, [TBA(Cl)] = 0.1 M. Glassy carbon and Pt wire were used as working and counter electrodes, respectively.

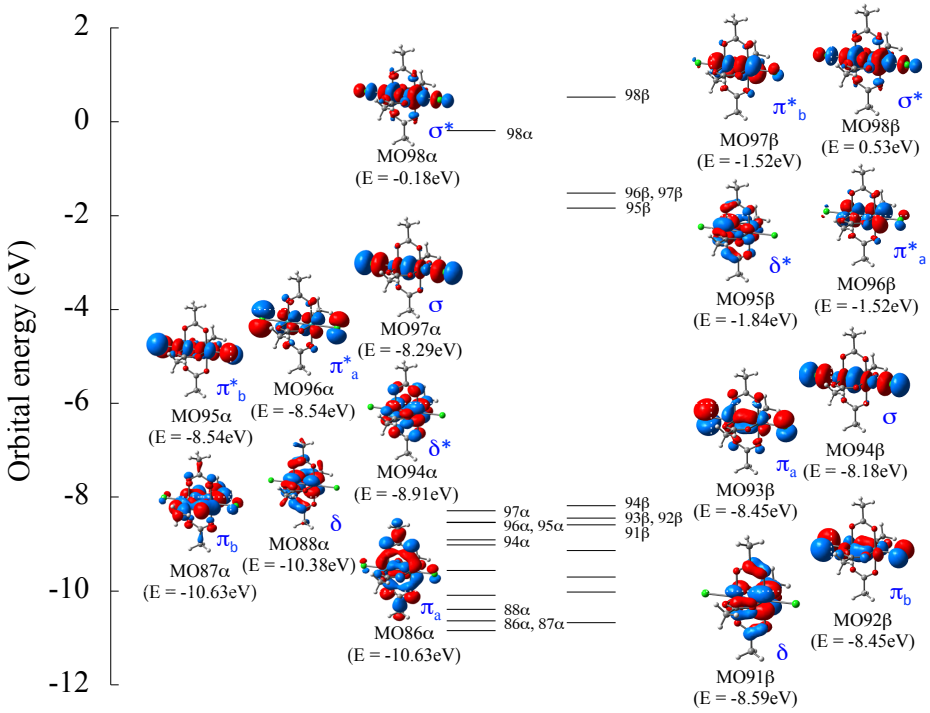

Fig. S10. Selected MOs of $[Ru_2(O_2CCH_3)_4Cl_2]^-$. The bond characters, σ (σ^*), π (π^*), and δ (δ^*), based on the direct Ru-Ru interaction are described with the blue colored letters.