Supporting Information

Aggregation of chiral hexanuclear complex-cations into cationic metallosupramolecules with concomitant aggregation of inorganic counter-anions into anionic clusters

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Experimental Procedures

[Au$_2$(dppe)(D-Hpen)$_2$] ([1]). To a white suspension containing 1.0 g (1.2 mmol) of [(AuCl)$_2$(dppe)] in 120 mL of EtOH was added 0.36 g (2.4 mmol) of D-H$_2$pen and 24 mL of a 0.1 M KOH aqueous solution. The mixture was stirred at room temperature for 2 h, and the resulting colorless solution was evaporated to dryness. The obtained white powder was recrystallized from EtOH/water (1:1), and the resulting colorless crystals of [**1**]·8H$_2$O were collected by filtration. Yield: 1.04 g (80 %). Anal. Calcd for [Au$_2$(dppe)(D-Hpen)$_2$]·8H$_2$O = $C_{36}H_{60}N_2O_{12}P_2S_2Au_2$: C, 35.07; H, 4.91; N, 2.27%. Found: C, 35.19; H, 4.72; N, 2.27%. IR (KBr, cm^{-1}): 1627 (COO$^-$), 1104, 693, 523 (P–Ph).

[Au$_4$Co$_2$(dppe)$_2$(D-pen)$_4$]Cl$_2$ ([2]Cl$_2$). To a suspension containing [**1**]·8H$_2$O (50 mg, 0.04 mmol) in EtOH/water (1:1, 6 mL) was added Co(OAc)$_2$·4H$_2$O (10 mg, 0.04 mmol) and PbO$_2$ (100 mg, 0.42 mmol), which was stirred at room temperature for 2 h. After removal of the unreacted PbO$_2$ by filtration, a 0.1 M NaCl aqueous solution (1.2 mL) was added to the purple-brown filtrate. Purple crystals of the [**2**]Cl$_2$ were obtained by slow evaporation at room temperature for 3 days. Yield: 45 mg (92 %). Anal. Calcd for [Au$_4$Co$_2$(dppe)$_2$(D-pen)$_4$]Cl$_2$·10H$_2$O = $C_{72}H_{92}N_4O_{12}P_4S_4Cl_2Co_2Au_4$: C, 34.01; H, 4.12; N, 2.20%. Found: C, 33.96; H, 4.19; N, 2.15%. IR (KBr, cm^{-1}): 1652 (COO$^-$), 1104, 693, 520 (P–Ph).

[Au$_4$Co$_2$(dppe)$_2$(D-pen)$_4$](ClO$_4$)$_2$ ([2](ClO$_4$)$_2$). To a suspension containing [**1**]·8H$_2$O (50 mg, 0.04 mmol) in EtOH/water (1:1, 6 mL) was added Co(OAc)$_2$·4H$_2$O (10 mg, 0.04 mmol) and PbO$_2$ (100 mg, 0.42 mmol), which was stirred at room temperature for 2 h. After removal of the unreacted PbO$_2$ by filtration, a 0.1 M NaClO$_4$ aqueous solution (1.2 mL) was added to the purple-brown filtrate. Purple crystals of the [**2**](ClO$_4$)$_2$ were obtained by slow evaporation at room temperature for 3 days. Yield: 36 mg (72%). Anal. Calcd for [Au$_4$Co$_2$(dppe)$_2$(D-pen)$_4$](ClO$_4$)$_2$·6H$_2$O = $C_{72}H_{96}N_4O_{22}P_4S_4Cl_2Co_2Au_4$: C, 33.28; H, 3.72; N, 2.16%. Found: C, 33.28; H, 3.60; N 2.21%. IR (KBr, cm^{-1}): 1656 (COO$^-$), 1107, 627 (ClO$_4^-$), 693, 519 (P–Ph).

X-ray Structural Determinations. Single-crystal X-ray diffraction experiments for [**2**]Cl$_2$·11H$_2$O and [**2**](ClO$_4$)$_2$·4.67H$_2$O were performed on a Rigaku RAXIS-RAPID imaging plate area detector with graphite-monochromated Mo Kα radiation at –73 °C. The measurements were performed just after picking up each crystal from the reaction solution. The intensity data were collected by the ω scan technique and were empirically corrected for absorption.
Crystal data for [**2**]Cl$_2$·11H$_2$O: Rigaku RAXIS-RAPID, T = 200 K, Mo Kα radiation (λ = 0.71073 Å). $C_{72}H_{106}Au_4Cl_2Co_2N_4O_{19}P_4S_4$, M = 2560.35, cubic, space group $F23$, a = 38.0216(6) Å, V = 54965.6(15)

Å^3, Z = 24, ω scan mode, $2\theta_{\text{max}}$ = 55.0°, 134160 reflections collected, 10478 independent reflections, 9339 observed reflections ($I > 2\sigma(I)$), $R1$, w$R2$ ($I > 2\sigma(I)$) = 0.047, 0.134, $R1$, w$R2$ (all data) = 0.054, 0.139, Flack parameter 0.044(7). Crystal data for [**2**]$(ClO_4)_2\cdot4.67H_2O$: Rigaku RAXIS-RAPID, T = 200 K, Mo Kα radiation (λ = 0.71073 Å). $C_{72}H_{89.33}Au_4Cl_2Co_2N_4O_{20.67}P_4S_4$, M = 2570.22, cubic, space group F23, a = 38.4167(8) Å, V = 56697(2) Å^3, Z = 24, ω scan mode, $2\theta_{\text{max}}$ = 55.0°, 138137 reflections collected, 10786 independent reflections, 4446 observed reflections ($I > 2\sigma(I)$), $R1$, w$R2$ ($I > 2\sigma(I)$) = 0.054, 0.134, $R1$, w$R2$ (all data) = 0.066, 0.144, Flack parameter 0.006(8).

The structures were solved by direct methods using SHELXS-97. The structure refinements were carried out using full-matrix least-squares (SHELXL-97). For [**2**]$Cl_2\cdot11H_2O$, a half hexanuclear cation, chloride anions and water molecules were crystallographically independent. The non-hydrogen atoms except for the disorder atoms were refined anisotropically, while the others were refined isotropically. H atoms were included in calculated positions except those of water molecules. SIMU restraints, which restrain the displacement parameters for spatially adjacent atoms, were used to model two phenyl rings. For [**2**]$(ClO_4)_2\cdot4.67H_2O$, a half hexanuclear cation, disordered perchlorate anions, and water molecules were crystallographically independent. The non-hydrogen atoms except for the disorder atoms were refined anisotropically, while the others were refined isotropically. H atoms were included in calculated positions except those of water molecules. DFIX restrains, which restrain the distances to target values (Cl–O = 1.41 Å and O–O = 2.29 Å), were used to model perchlorate anions. Anisotropically refined perchlorate anions were modeled using SIMU restraints, and disordered isotropically refined perchlorate anions were modeled using EADP constraints to have the same displacement parameters. SIMU restraints were used to model one phenyl ring.

For [**2**]Cl_2, the number of the water molecules is slightly larger than that calculated from elemental analysis. This is most likely due to the partial removal of water molecules from the compound before its elemental analysis was carried out. For [**2**]$(ClO_4)_2$, the number of the water molecules is smaller than that calculated from elemental analysis. This is most likely due to the presence of water molecules in the void space, which are not detectable by X-ray analysis because of their severe disorder.

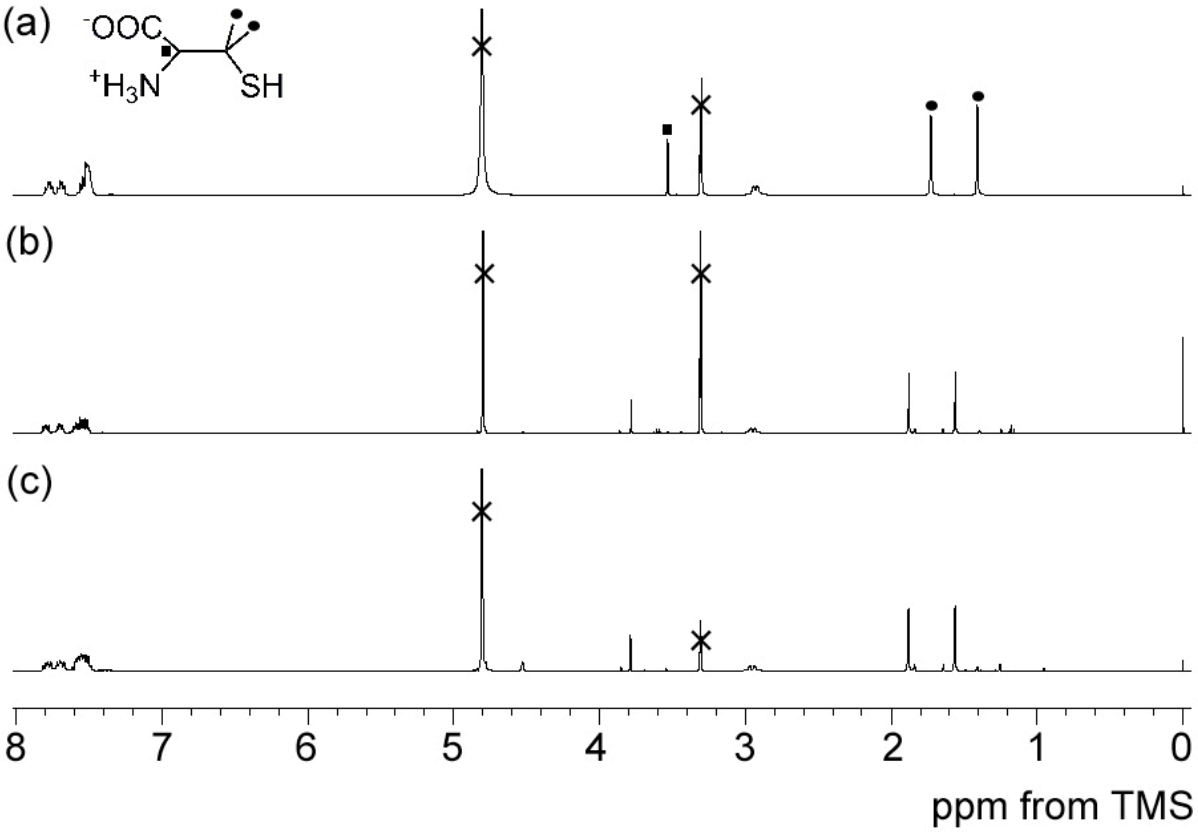

Fig. S1 ^{1}H NMR spectra of (a) [**1**], (b) [**2**]Cl_2 and (c) [**2**]$(ClO_4)_2$ in CD_3OD.

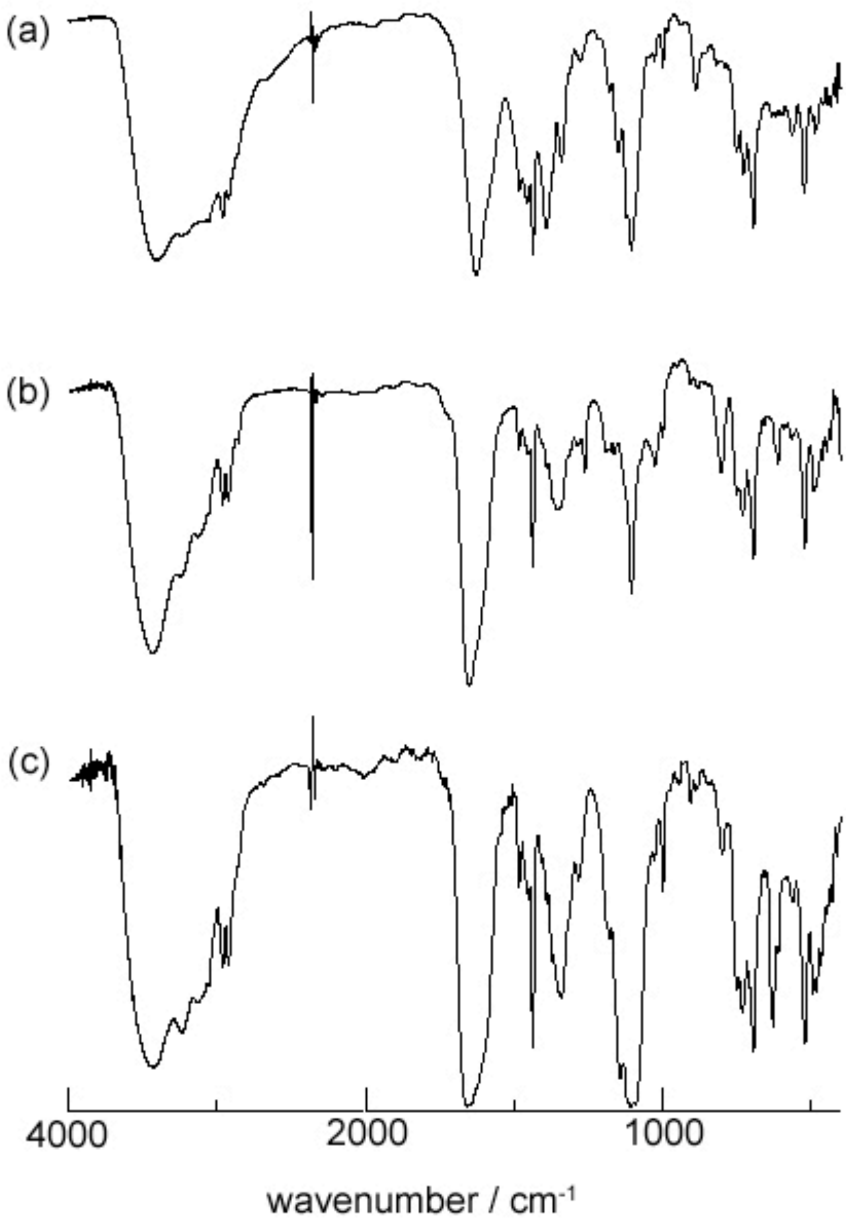

Fig. S2 IR spectra of (a) [**1**], (b) [**2**]Cl_2 and (c) [**2**]$(ClO_4)_2$ (KBr disks).

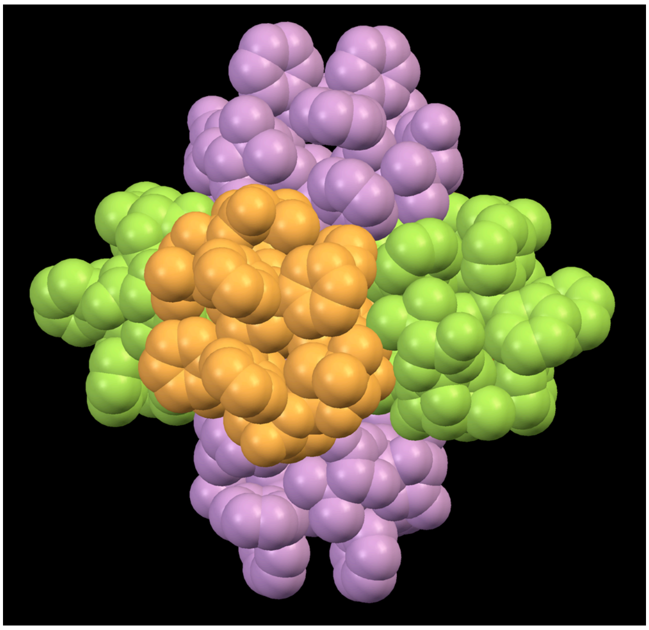

Fig. S3 Octahedron-shaped supramolecular structure in ([**2**]$^{2+}$)$_6$.

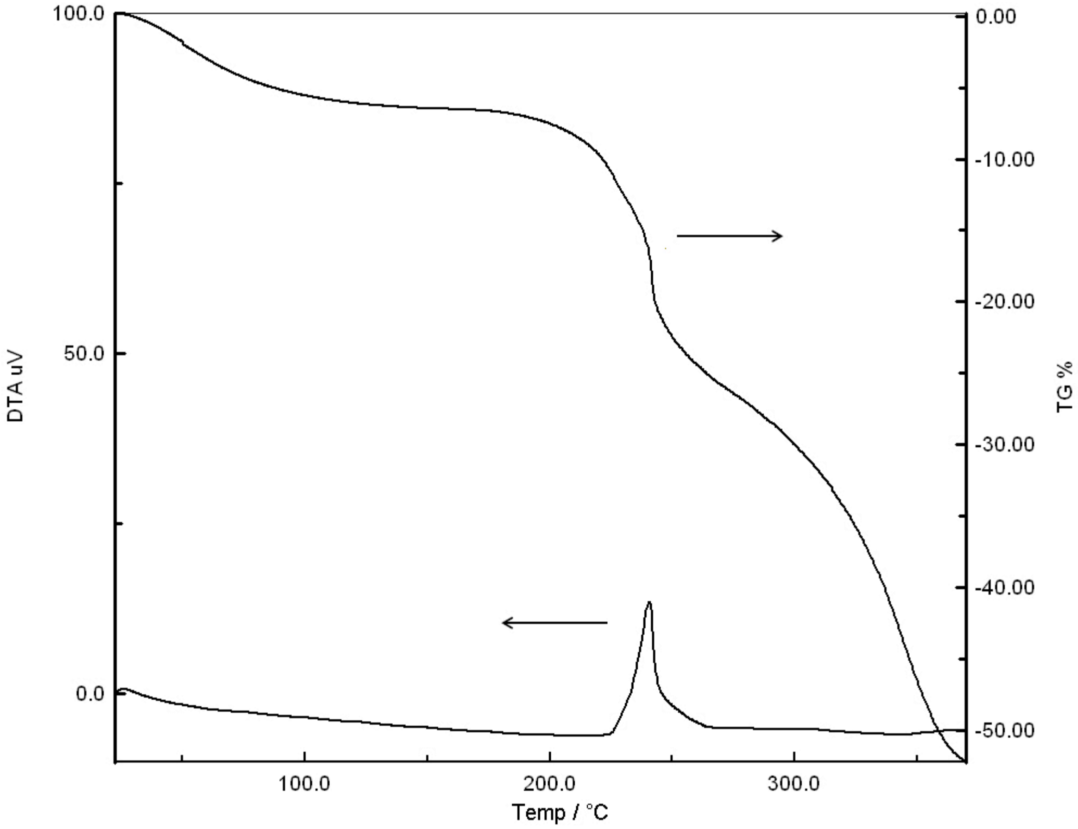

Fig. S4 TG/DTA diagram for [**2**]($(ClO_4)_2$).

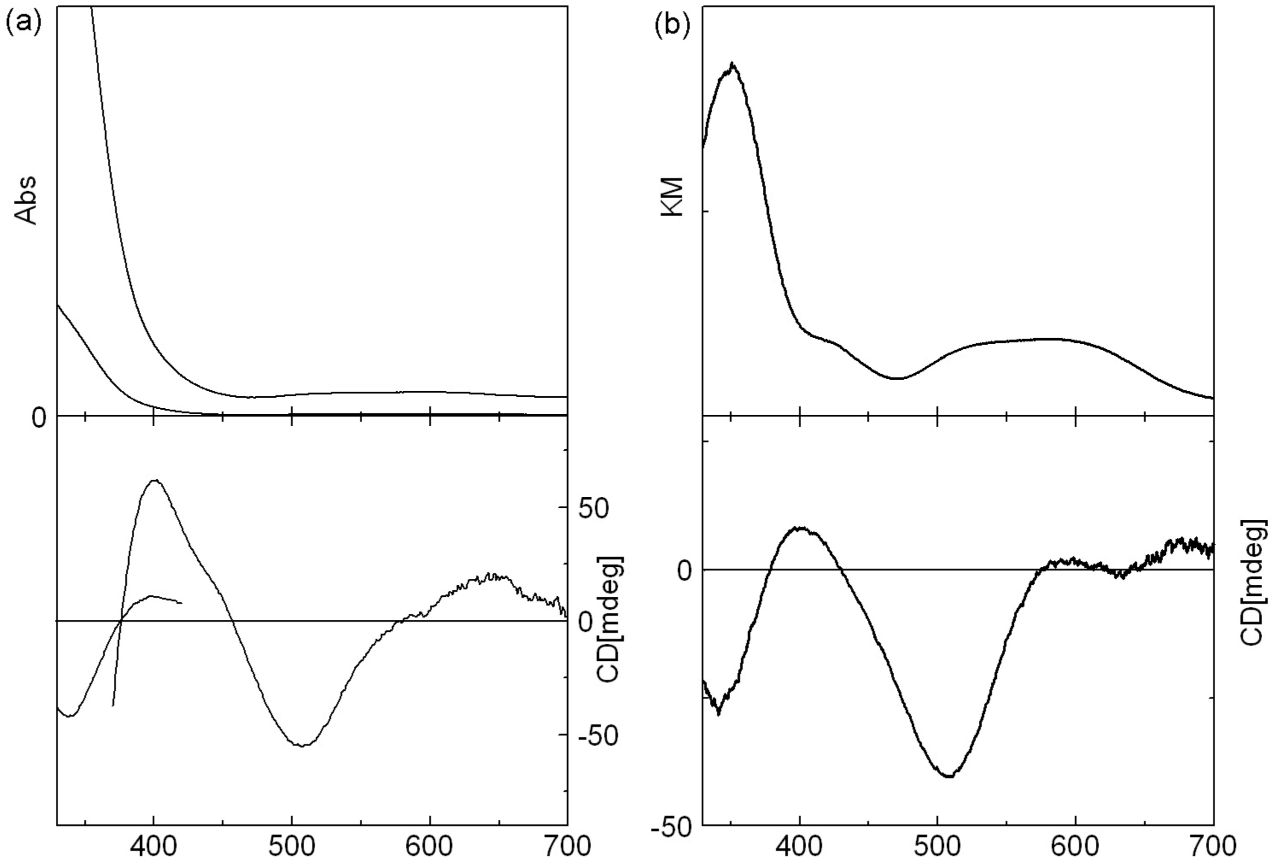

Fig. S5 (a) Absorption and CD spectra of [**2**]$(ClO_4)_2$ in MeOH and (b) reflection and CD spectra of [**2**]$(ClO_4)_2$ in the solid state.