Supplementary Materials

Noncentrosymmetric Supramolecular Hydrogen bonded Assemblies Based on Achiral Pyrazine-Bridged Zinc(II) Coordi-nation Polymers with Pyrazinedione Derivatives

Ko Yoneda, Ken Kanazashi, Hitoshi Kumagai, Ryuta Ishikawa and Satoshi Kawata

Experimental Section

Materials and Methods.

Zn(OAc)$_2$·2H$_2$O, Co(OAc)$_2$·4H$_2$O, and EtOH were purchased from Wako Pure Chemical Industries, Ltd..　pyz and H$_2$CN$_2$pyzdione were purchased from Tokyo Chemical Industry (TCI) Co., Ltd..　All chemicals were of reagent grade and used as received.　All the synthetic reactions and manipulations were performed under aerobic conditions at room temperature.

Synthesis.

[Zn(H$_2$O)$_6$][Zn(H$_2$CN$_2$pyzdione)$_2$(pyz)]·6H$_2$O (1)

A suitable crystal for X-ray diffraction measurement was grown by using a liquid-liquid slow diffusion technique, wherein each reactant diffused in straight glass tubes with ϕ 8 mm, leading to the growth of the crystals on the walls of the glassware. Two stock solutions of Zn(OAc)$_2$·2H$_2$O and H$_2$CN$_2$pyzdione in H$_2$O (20 mmol L^{-1}) and pyz in EtOH (10 mmol L^{-1}) were prepared separately.　On top of a pale yellow solution of Zn(OAc)$_2$·2H$_2$O and H$_2$CN$_2$pyzdione in 2 mL of H$_2$O was carefully layered a colorless solution of pyz in 2 mL of EtOH.　The glass tube was sealed left undisturbed.　Colorless prismatic crystals began to form after several days. The diffusion was complete in one week.　Crystals were separated from the glass tube, washed with a small amount of cold H$_2$O, and dried in air.　Yield: 62%. Anal. Calc. for C$_{16}$H$_{28}$Zn$_2$N$_{10}$O$_{16}$: C, 25.72; H, 3.78; N, 18.75.　Found: C, 25.69; H, 3.70; N, 18.50. FTIR (KBr): ν_{CO} = 1510, ν_{CN} = 2226 cm^{-1}.

[Co(H$_2$O)$_6$][Co(H$_2$CN$_2$pyzdione)$_2$(pyz)]·6H$_2$O (2)

This compound was synthesized by using the same method as that for 1 with Co(OAc)$_2$·4H$_2$O instead of Zn(OAc)$_2$·2H$_2$O. Yield: 74%.　Anal. Calc. for C$_{16}$H$_{28}$Co$_2$N$_{10}$O$_{16}$: C, 26.17; H, 3.84; N, 19.07. Found: C, 26.24; H, 3.78; N, 18.92. FTIR (KBr): ν_{CO} = 1508, ν_{CN} = 2228 cm^{-1}.

X-ray Crystallography.

Single crystals of **1** and **2** were coated with Nujol, quickly mounted on MicroLoops, and immediately cooled in a cold dinitrogen stream to prevent any interstitial solvent loss. Data collections were performed on a Rigaku R-AXIS RAPID II Imaging Plate (IP) diffractometer equipped with a graphite-monochromated Mo Kα radiation (λ = 0.71075 Å) and a low-temperature apparatus. Integrated data were corrected for absorption using multi-scan methods, the structure was solved by direct methods and refined against F^2 using least squares techniques. Preliminary data analysis, data integration, and absorption collections were performed on a Rigaku RAPID AUTO software package. The molecular structures were solved by the direct methods SIR2011 for **1** and SHELXT-2014 for **2**, and refined by full least-squares on all F^2 data (SHELXL-2014 for **1** and **2**) using a Rigaku CrystakStructure 4.0 software package. All non-H atoms were refined anisotropically. H atoms on pyz ligands were included in calculated positions using a riding model. On the other hand, H atoms of aquo ligands and interstitial H_2O molecules were found in Fourier difference maps and refined isotropically, which were also constrained to ride on their parent atoms with O–H distances of 0.85 Å and H–O–H angles of 103°. Some interstitial H_2O molecules in **2** were disordered over two positions with a site occupancy of 0.5 for O6 and O7 atoms. The Bravais lattice for both **1** and **2** is primitive monoclinic with systematic absences indicating the space group to be either $C2$ or $C2/m$. Centricity analyses carried out with the Rigaku CrystakStructure 4.0 software confirm that **2** has a crystallographic inversion center, with $|E^2 - 1|$ value of 0.930, while that of **1** is 0.835, where theoretical $|E^2 - 1|$ values are 0.968 and 0.736 for centrosymmetric and noncentrosymmetric space group, respectively. From $|E^2 - 1|$ value of 0.835 for **1**, it was difficult to determine whether centrosymmetric or noncentrosymmetric. Attempts to solve the molecular structure of **1** as the centrosymmetric space group $C2/m$ were not successful at all, but the molecular structure could be completely solved as $C2$ without any difficulties to give final $R[F^2 > 2 \ (F^2)]$ and $wR(F^2)$ values of 0.0199 and 0.0525. Therefore, we concluded that the space group of **1** is unambiguously $C2$. Pertinent crystallographic details of both **1** (CCDC 1969750) and **2** (CCDC 1969761) have been deposited with The Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif. Selected crystallographic data for **1** and **2** are given in Table S1.

Powder X-ray Diffraction (PXRD) Measurement.

Freshly prepared crystals were finely crushed with a mortar and pestle in the mother liquor. These ground-powdered samples were immediately loaded on Si-based reflection free sample holders with a depth of 0.2 mm. All PXRD data were collected with a Rigaku SmartLab automated multipurpose diffractometer (40 kV/30 mA; 1.2 kW) using Cu Kα radiation (λ = 1.5406 Å) equipped with an automated variable-temperature stage for in-situ PXRD measurements in the temperature range of 90–500 K at a scan step size of 0.02°. Calculated PXRD patterns were implemented by using CrystalDiffract software.

Thermal Gravimetric Analysis (TGA).

TGA data were collected on a Seiko Instruments SSC5200 Thermo Analyzer at a heating rate of 10 K min^{-1} in the temperature range of 300–450 K under a continuous dinitrogen stream.

Differential Scanning Calorimetry (DSC).

DSC measurements were carried out a Seiko Instruments SSC6300 Thermo Analyzer at a heating rate of 10 K min^{-1} in the temperature range of 300–450 K under a continuous dinitrogen stream.

Diffuse Reflectance Spectroscopy.

Diffuse reflectance spectra were collected at room temperature using a JASCO UV/VIS/NIR V-570 spectrometer equipped with an integrating sphere in the range of 220–800 nm. $BaSO_4$ powder was used as a non-adsorbing matrix.

Circular Dichroism Spectroscopy.

CD spectra were collected on KBr disks using a JASCO J-600 spectropolarimeter equipped with a temperature control apparatus.

Other Physical Measurements.

CHN Elemental analyses were performed on a Micro Corder JM10 (J-Science Lab Co., Ltd.).　FTIR spectra were collected at room temperature on KBr disks using a JASCO FT/IR-410 spectrometer in the range of 400–4000 cm^{-1}.

Table S1 Summary of crystal data for **1** and **2**

	1	2
Empirical formula	$C_{16}H_{28}Zn_2N_{10}O_{16}$	$C_{16}H_{28}Co_2N_{10}O_{16}$
Formula weight (g mol^{-1})	747.26	734.34
Temperature (K)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic
Space group	$C2$	$C2/m$
a (Å)	20.5028(9)	20.4843(9)
b (Å)	7.0797(3)	7.0622(3)
c (Å)	10.0831(5)	10.0915(5)
β (°)	93.0344(18)	92.8986(13)
V (Å^3)	1461.55(11)	1458.01(11)
Z	2	2
D_{calcd} (Mg m^{-3})	1.698	1.673
μ (mm^{-1})	1.729	1.226
$F(000)$	764	752
Crystal color, shape	colorless, prism	orange, plate
Crystal size (mm)	$0.44 \times 0.20 \times 0.20$	$0.70 \times 0.40 \times 0.05$
θ range (°)	3.0–27.5	3.1–27.5
Index ranges	$h = -26 \rightarrow 26, k = -9 \rightarrow 8,$ $l = -13 \rightarrow 13$	$h = -24 \rightarrow 26, k = -9 \rightarrow 9,$ $l = -13 \rightarrow 13$
R_{int}	0.015	0.039
No. of reflections	2974	1798
No. of parameters	249	167
No. of restraints	18	15
$R[F^2 > 2.0\sigma(F^2)]$	0.0199	0.0378
$wR(F^2)$	0.0525	0.1000
S	1.109	1.197
$\Delta\rho_{min}, \Delta\rho_{max}$ (e Å^{-3})	–0.37, 0.28	–0.33, 0.97
Absolute structure parameter	0.019(5)	
CCDC number	1969750	1969761

Table S2 Selected bond distances and angles for **1**.

atom	atom	distance	atom	atom	distance
Zn1	O1	2.1269(11)	Zn1	O2	2.0912(12)
Zn1	N5	2.146(3)	Zn1	N6	2.159(3)
Zn2	O3	2.0783(13)	Zn2	O4	2.0970(17)
Zn2	O5	2.0762(18)			

atom	atom	atom	angle	atom	atom	atom	angle
O2^{i}	Zn1	O2	179.82(12)	O5	Zn2	O3	92.27(9)
O2^{i}	Zn1	O1	100.66(4)	O5^{iii}	Zn2	O3	88.16(8)
O2	Zn1	O1	79.34(4)	O3^{iii}	Zn2	O3	179.39(18)
O1	Zn1	O1^{i}	178.81(9)	O3	Zn2	O4^{iii}	90.84(8)
O2	Zn1	N5	89.91(6)	O5	Zn2	O4	178.97(8)
O1	Zn1	N5	90.60(4)	O5^{iii}	Zn2	O4	91.35(6)
O2	Zn1	N6^{ii}	90.09(6)	O3^{iii}	Zn2	O4	90.84(8)
O1	Zn1	N6^{ii}	89.40(4)	O3	Zn2	O4	88.72(9)
O5	Zn2	O5^{iii}	88.42(10)	O4^{iii}	Zn2	O4	88.91(10)

Symmetry Operators:

(i) $-x+1, y, -z+1$ (ii) $-x+1, y, -z$

(iii) $-x, y, -z$

Table S3 Selected bond distances and angles for **2**.

atom	atom	distance	atom	atom	distance
Co1	O1	2.131(2)	Co1	O2	2.075(2)
Co1	N5	2.144(2)	Co2	O3	2.063(2)
Co2	O4	2.0915(16)			

atom	atom	atom	angle
O2	Co1	O1	79.11(8)
O3	Co2	O4^{ii}	91.73(6)
O4^{ii}	Co2	O4^{iii}	90.31(9)

Symmetry Operators:
(i) $-x+1, -y+1, -z+1$ (ii) $-x+1, -y+1, -z$
(iii) $-x+1, y, -z$

Table S4. Hydrogen-bond distances (Å) and geometries (°) for **1**.

D–H$\cdots A$	D–H	H$\cdots A$	$D\cdots A$	D–H$\cdots A$
O3–H3A$\cdots$O1	0.85	1.932	2.760(2)	164.6
O4–H4A$\cdots$O2^{i}	0.85	2.105	2.866(2)	148.9
O5–H5A$\cdots$O2^{ii}	0.85	1.934	2.729(2)	155.7
O3–H3B$\cdots$O8	0.85	1.950	2.715(2)	149.2
O4–H4B$\cdots$O6^{iii}	0.85	1.943	2.780(2)	168.0
O5–H5B$\cdots$O6^{iv}	0.85	1.885	2.734(3)	173.4
O7–H7B$\cdots$N1	0.85	2.056	2.888(2)	166.5
O8–H8A$\cdots$N2^{ii}	0.85	1.979	2.817(2)	167.9
O6–H6B$\cdots$N4^{ii}	0.85	2.171	3.001(2)	165.4
O6–H6A$\cdots$O7	0.85	1.947	2.781(2)	167.1
O7–H7A$\cdots$O8	0.85	1.849	2.690(2)	169.4
O8–H8B$\cdots$O7^{v}	0.78	1.955	2.732(3)	176.1

Symmetry codes: (i) $-x+1, y, -z+1$, (ii) $x, y, z-1$, (iii) $x+1/2, y+1/2, z$, (iv) $-x+1/2, y-1/2, -z$, and (v) $-x+1/2, y+1/2, -z$.
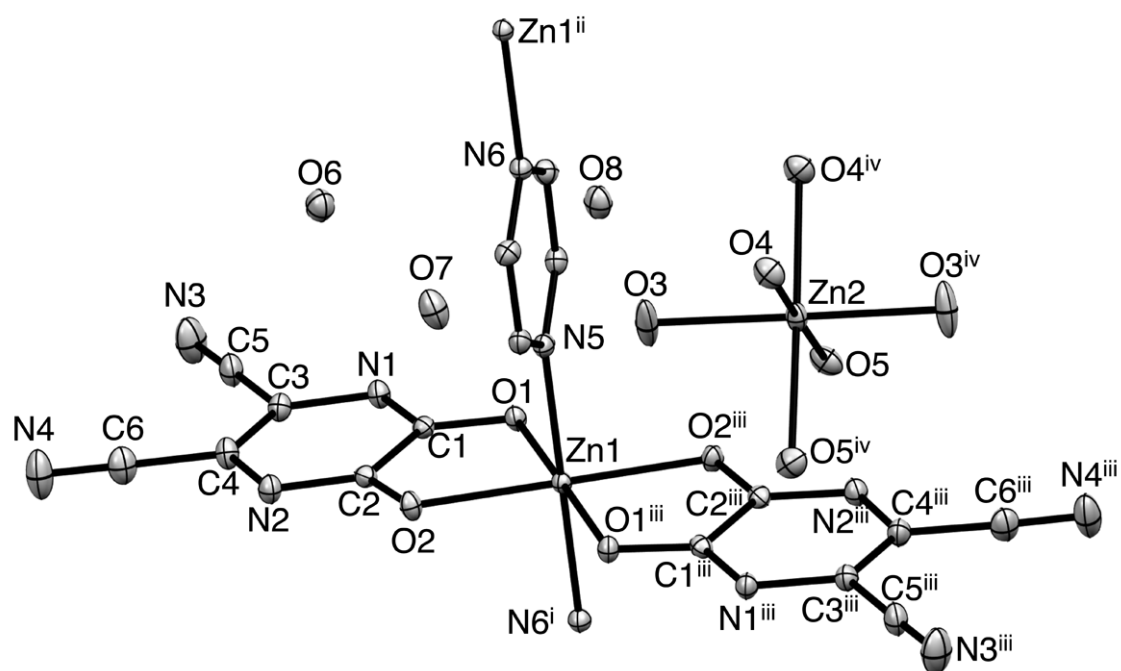
Table S5. Hydrogen-bond distances (Å) (°) and geometries (°) for **2**.

D–H$\cdots A$	D–H	H$\cdots A$	$D\cdots A$	D–H$\cdots A$
O3–H3A$\cdots$O1	0.85	1.916	2.757(3)	170.2
O4–H4A$\cdots$O2^{i}	0.85	2.012	2.798(2)	153.7
O3–H3B$\cdots$O7^{ii}	0.85	1.950	2.728(2)	151.7
O4–H4B$\cdots$O5^{iii}	0.85	1.914	2.759(2)	173.9
O5–H5A$\cdots$N4^{iv}	0.85	2.166	2.981(4)	160.2
O5–H5B$\cdots$ O6	0.85	1.944	2.774(4)	164.8
O6–H6A$\cdots$O7	0.85	1.869	2.450(5)	124.5
O6–H6B$\cdots$ N1	0.85	2.246	2.913(4)	135.5
O7–H7A$\cdots$N2^{iv}	0.85	2.107	2.774(4)	135.0
O7–H7B$\cdots$ O6^{v}	0.85	1.938	2.725(5)	153.8

Symmetry codes: (i) –x+1, –y+1, –z+1, (ii) x, –y+1, z, (iii) x+1/2, y+1/2, z, (iv) x, y, z–1, and (v) –x+1/2, –y+1/2, –z.

Figure S1 Coordination around the zinc atoms and the adopted atom numbering for **1**. Ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Symmetry codes: (i) $x, y–1, z$, (ii) $x, y+1, z$, (iii) $–x+1, y, –z+1$, (iv) $–x+1, y, –z$.
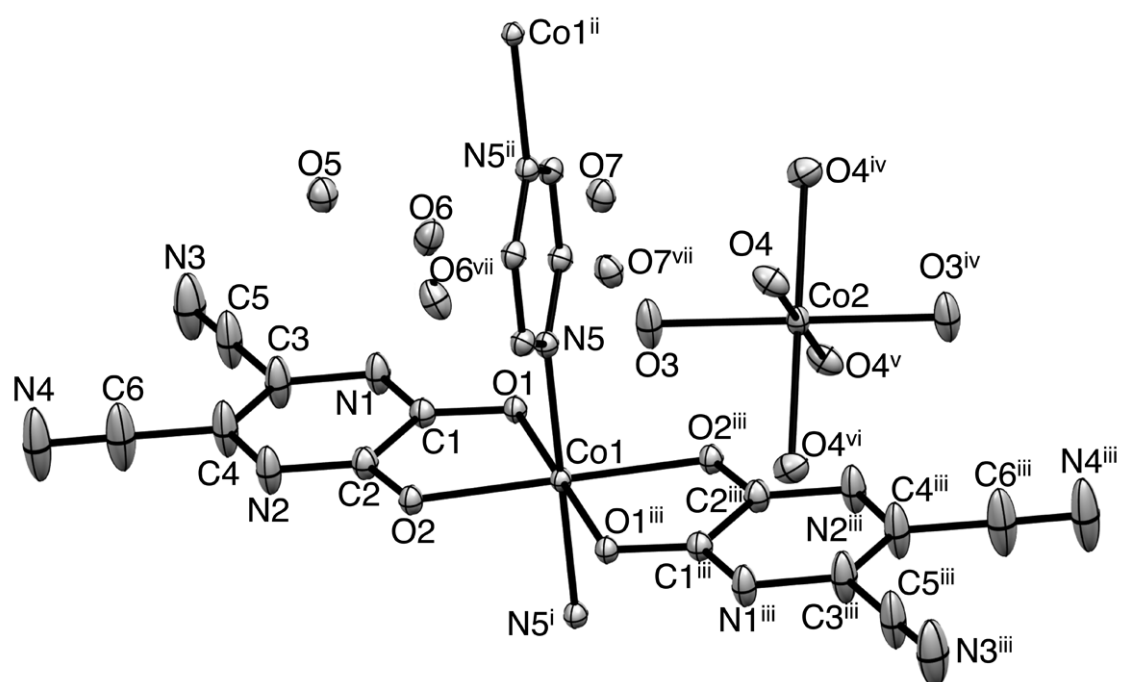
Figure S2 Coordination around the cobalt atoms and the adopted atom numbering for **2**. Ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Symmetry codes: (i) $-x+1$, $-y+1$, $-z+1$, (ii) x, $-y+2$, z, (iii) $-x+1$, y, $-z+1$, (iv) $-x+1$, y, $-z$, (v) $-x+1$, $-y+1$, $-z$, (vi) x, $-y+1$, z, (vii) x, $-y+1$, z.

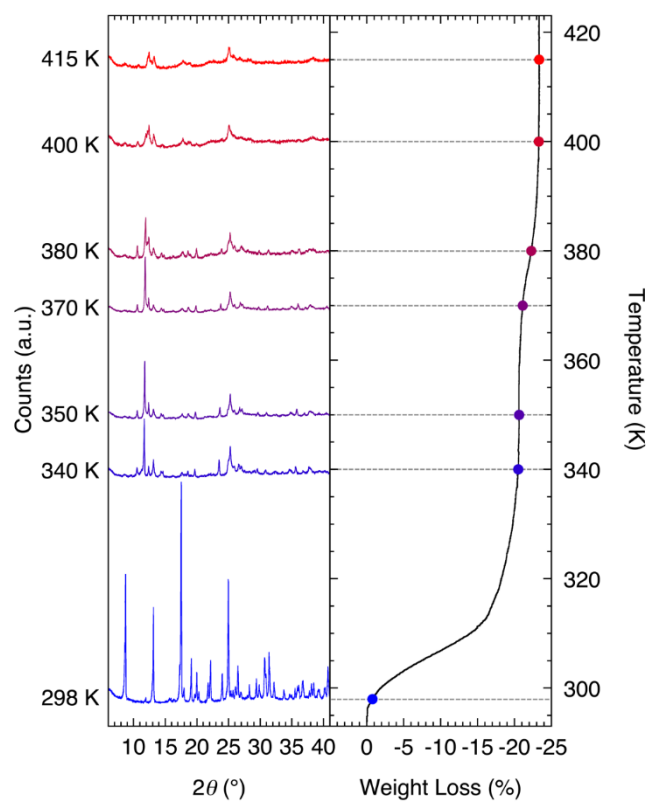Figure S3.   TGA and differential thermal analysis (DTA) data for **1**.

Figure S4. In situ variable temperature PXRD patterns (left) at given temperatures and TGA data (right) for **1**.
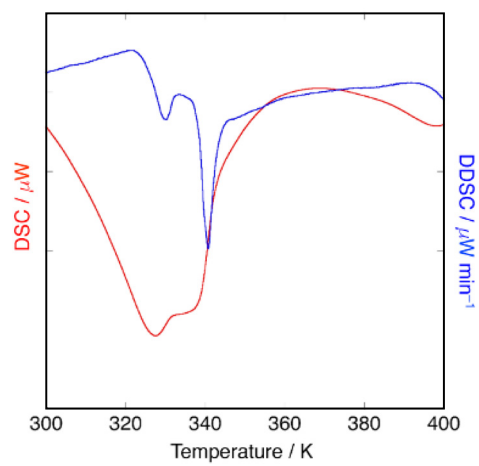
Figure S5. Results of DSC measurement and time derivative of DSC (DDSC).
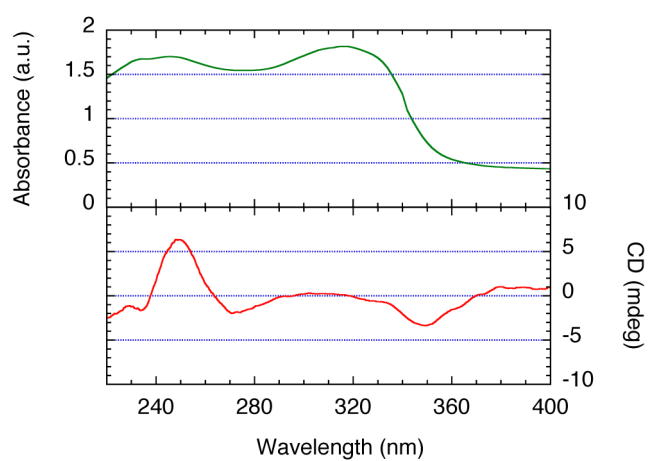
Figure S6. Solid state diffuse reflectance (green solid line) and CD (red solid line) spectra of **1** in the UV region at room temperature.