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An Unprecedented 2-D Cluster Polymer Constructed from Unique Mixed-valence $Cu^{I}_{6}Cu^{II}_{6}$ Subunits

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Supplementary Information

Experimental Section

Materials and Methods

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. IR Spectra were recorded on a Nicolet NEXUS 470-FTIR spectrophotometer as KBr pellets in the 400-4000 cm^{-1} region. Elemental analyses (C, H and N) were carried out on a FLASH EA1112 Elemental Analyzer. Diffraction intensity data for single crystals of **1a** and **1b** was collected at room temperature on a Rigaku Saturn CCD diffractometer equipped with graphite monochromated Mo*Ka* (λ = 0.71073Å). Diffraction intensity data for single crystals of **1c** and **2** was collected at room temperature on a Bruker SMART APEXII CCD diffractometer equipped with graphite monochromated Mo*Ka* (λ = 0.71073Å). TG-DSC measurements were performed by heating the sample from 20 to 1000°C at a rate of 10°C·min^{-1} in air on a Perkin Elmer DTA-7 differential thermal analyzer. The phase purity of the as-synthesized products were examined by X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.54187 Å). The morphology and size of the obtained products were further observed by a field-emission microscope (JEOl-JSM-6700F 25KV). The X-ray photoelectron spectroscopy spectra were recorded on a PHI5300 and Electron Spin Resonance Spectrometer (EPR) were recorded on JES-FA200.

Synthesis of {$[Pr_2(H_2L)_4(Phen)_2(NO_3)_2]\cdot CH_3OH$} (1a)

A mixture of $Pr(NO_3)_2\cdot 3H_2O$ (0.050 mmol), Phen (0.05 mmol) and

2-(3-benzoylthioureido)ethanoic acid (H_3L) (0.050 mmol) in 8 mL solution of methanol and water (v/v = 6:1). The mixture was put aside in room temperature for one week by slow evaporation. The quality green crystals for {$[Pr_2(H_2L)_4(Phen)_2(NO_3)_2]\cdot CH_3OH$} (**1a**) was obtained. Yield: 75.5%. IR(cm^{-1}, KBr): 3221m, 1668s, 1618s, 1615m 1425s, 1292s, 1172m, 1120w, 1028w, 974w, 895w, 847m, 780w, 726s, 664w, 529w, 464w. Anal. Calcd. for $C_{66}H_{60}N_{14}O_{20}S_4Pr_2$: C, 44.55; H, 3.40; N, 11.02%, S, 7.21%. Found: C, 44.11; H, 3.43; N, 11.32%, S, 7.33%.

Synthesis of {$[Ln_2(H_2L)_4(Phen)_2(NO_3)_2]\cdot CH_3OH$} (Ln = Nd (1b), or Ho (1c))

The dinuclear complexes **1b**, and **1c** were prepared in a manner similar to that described to **1a**. Lilac color block crystal were produced of {$[Nd_2(H_2L)_4(Phen)_4(NO_3)_2]\cdot CH_3OH$} (**1b**). Yield: 71.5%. IR (cm^{-1}, KBr): 3224(m), 1668(s), 1629(s), 1545(s), 1429(s), 1299(s), 1173(m), 1121(w), 975(m), 895(w), 849(w), 781(w), 727(s), 664(m), 467(w). Anal. Calcd. for $C_{66}H_{60}N_{14}O_{20}S_4Nd_2$: C, 44.38; H, 3.39; N, 10.98; S, 7.18%. Found: C, 44.35; H, 3.53; N, 11.27; S, 7.03%.

Pastel pink plate-like crystals of {$[Ho_2(H_2L)_4(Phen)_2(NO_3)_2]\cdot CH_3OH$} (**1c**) were recovered in 73.2% yield. IR (cm^{-1}, KBr): 3424(m), 1667(s), 1628(s), 1545(s), 1427(s), 1293(s), 1172(m), 1119(s), 1016(m), 974(m), 895(w), 848(w), 780(w), 724(s), 663(m), 626(w), 529(w), 464(w). Anal. Calcd. for $C_{66}H_{60}N_{14}O_{20}S_4Ho_2$: C, 43.38; H, 3.30; N, 10.73; S, 7.01%. Found: C, 43.35; H, 3.23; N, 10.47; S, 7.33%.

Synthesis of cluster polymer {$[Cu^I_6Cu^{II}_6L_6(H_2O)_3(CH_3OH)_6]\cdot 5H_2O\cdot 3CH_3OH$}$_n$ (2)

A solution of $Cu(OAc)_2\cdot H_2O$ (0.05 mmol) in methanol (10 mL) was added drop wise to a stirred solution of complex **1** (0.025 mmol) in DMF/H_2O mixture (v/v = 6:1) (10 mL) at 90°C. The resulting solution was stirring 10 min and filtered after cooling to room temperature. Dark-green single crystals of **2** were obtained by slow evaporation after two weeks. The reproducibility of the synthesis of compound **2** is good. Yield: 56.2%. IR(cm^{-1}, KBr): 3422 m, 1543.27s, 1464 s, 1436 m 1384 s, 1292 m, 1216 m, 1121 w, 1079 w, 895 w, 939 w, 732 w, 671 w, Anal. Calcd. for $C_{99}H_{113}N_{18}O_{46}S_9Cu_{18}$: C, 31.93; H, 3.08; N, 6.77%. Found: C, 31.52; H, 3.58; N, 6.52%.

Synthesis of Zn(II), Co(II)-exchanged products, {$[Cu^I_6Cu^{II}_5Zn(H_2O)_3(CH_3OH)_6]\cdot 5H_2O\cdot 3CH_3OH$}$_n$ (3) and

$\{[Cu^{I}_6Cu^{II}_4Co_2(H_2O)_3(CH_3OH)_6]\cdot 5H_2O\cdot 3CH_3OH\}_n$ (4).

Compounds **3** and **4** were prepared through respectively immersing big crystals of **2** into aqueous of 50 mg/ml $Zn(NO_3)_2$ and $Co(NO_3)_2$ for one week. Then the crystalline products **3** or **4** were filtered off, washed several times with water and methanol, and then dried in air. For **3**: IR (cm^{-1}, KBr): 3447m, 1626s, 1582m, 1543s 1465m, 1384m, 1217w. Anal. Calcd. $C_{69}H_{95}N_{12}O_{35}S_6Cu_{11}Zn$: C, 31.75; H, 3.64; N, 6.44%. Found: C, 31.41; H, 3.48; N, 6.53%. For **4**: IR(cm^{-1}, KBr): 3446m, 1623s, 1581w, 1543s, 1464m, 1385s, 1215w. Anal. Calcd. $C_{69}H_{95}N_{12}O_{35}S_6Cu_{10}Co_2$: C, 31.89; H, 3.66; N, 6.47%. Found: C, 31.61; H, 3.88; N, 6.62%

Crystallographic studies:

Crystal data and experimental details for complexes **1a-1c**, and **2** are contained in Table S1. Measurements of compounds **1a,** and **1b** were made on a Rigaku Saturn 724+ CCD diffractometer with a graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å). Complexes **1c** and **2** was measured on a BRUKER SMART APEX II CCD imaging plate area detector with graphite monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å). All data were collected at a temperature of 291(2) K using the ω-2θ scan technique and corrected for Lorenz-polarization effects. A correction for secondary extinction was applied. The structures were solved by direct methods and expanded using the Fourier technique. The non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were generated theoretically onto the specific carbon atoms and refined isotropically with fixed thermal factors. All calculations were performed using the SHELX-97 crystallographic software package. CCDC-730776, 730775 730774 and 730777 for complexes **1a**, **1b**, **1c** and **2**, respectively. Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk).

Thermogravimetric Analysis (TGA)

As shown in Figure S4, compounds **2**, **3** and **4** show very similar thermal behaviors. They all indicate complicated thermal decomposition process. This confirms that the three complexes have very similar morphology.

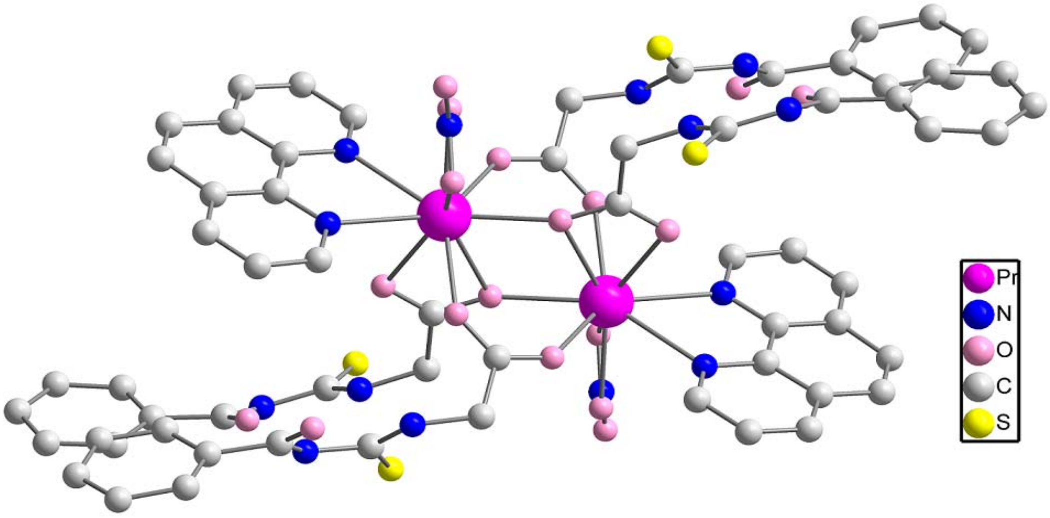

Fig. S1. X-ray molecular structure of **1a**

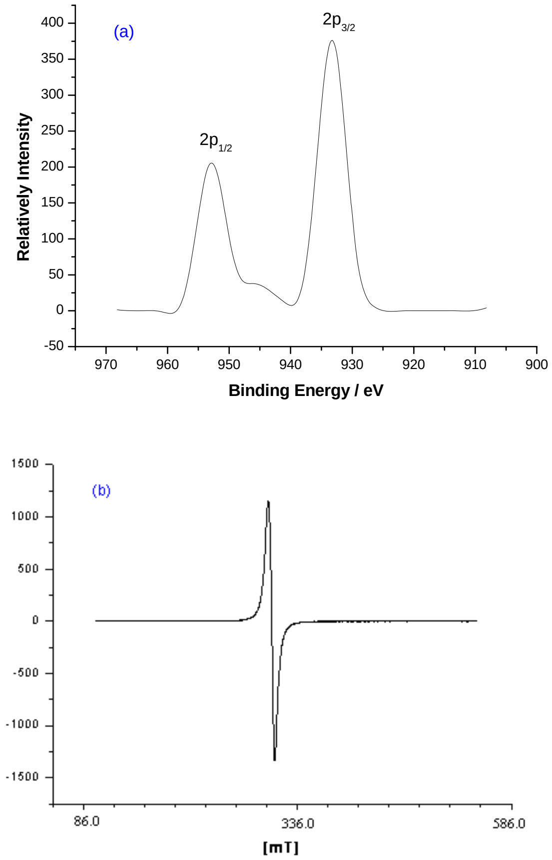

Fig. S2. (a) High-resolution XPS spectra of Cu in **2**; (b) EPR spectra of **2**.

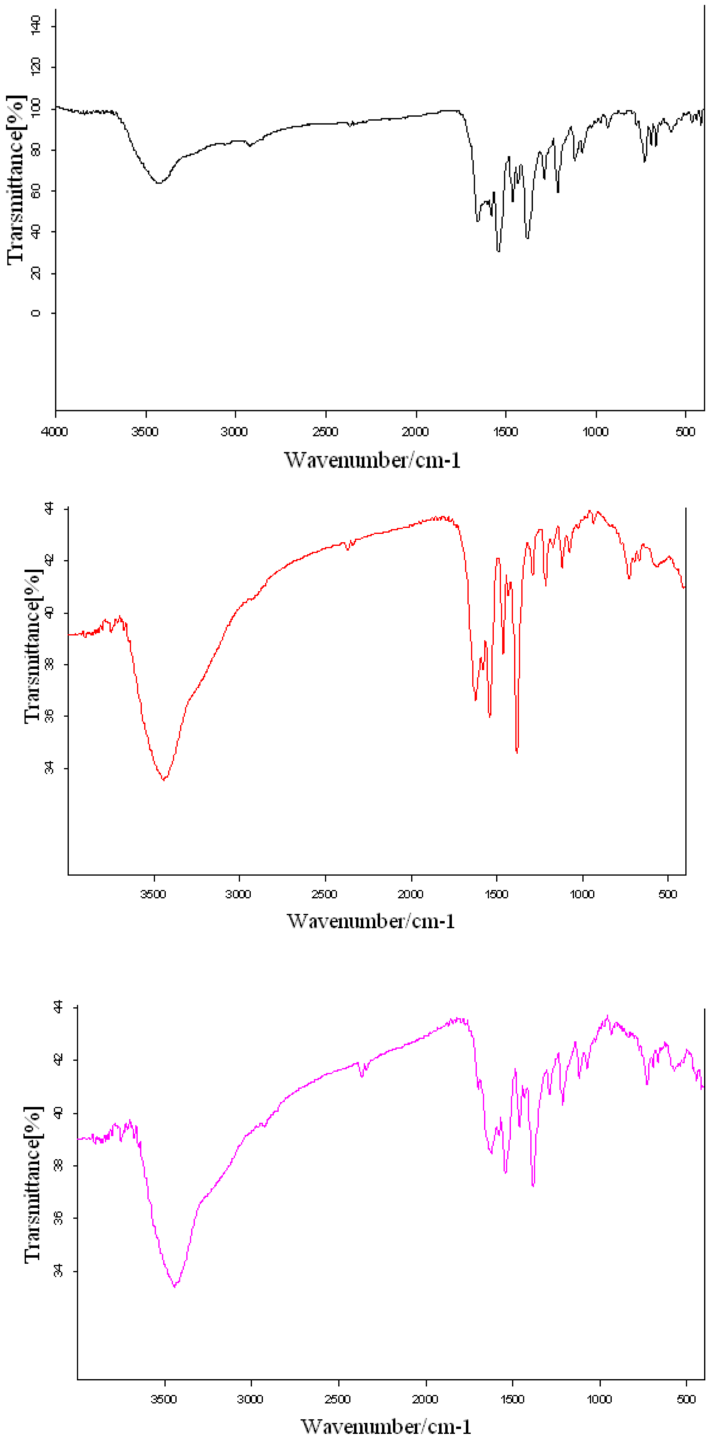

Fig. S3. Analogous IR spectra of **2** and its Zn-exchanged product **3**, Co-exchanged product **4**.

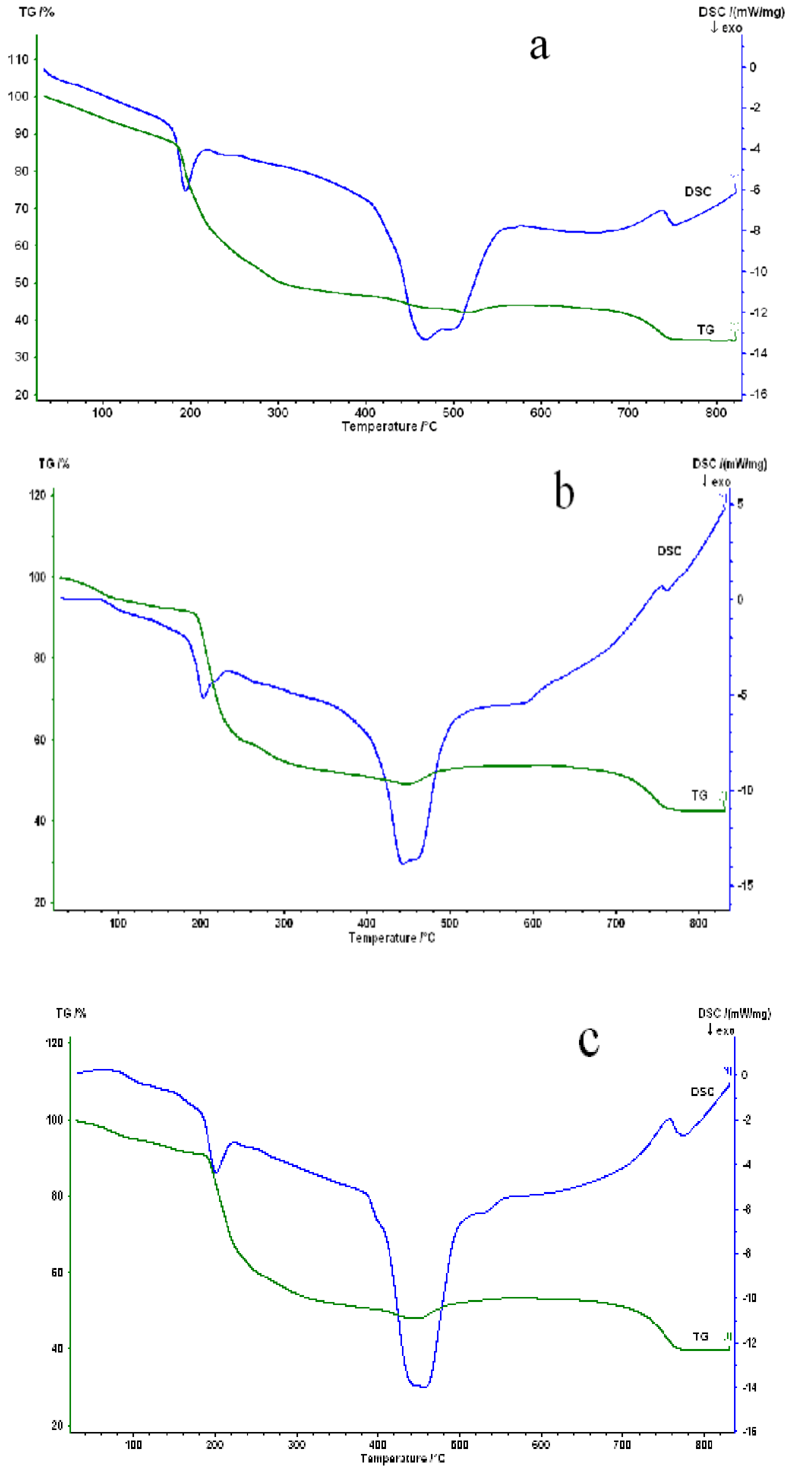

Fig. S4. TG and DSC analyses of **2** (a) and its Zn-exchanged product **3** (b), Co-exchanged product **4** (c).

Table S1 Crystallographic Data for Compounds **1a-1c and 2**.

	1a	**1b**	**1c**	**2**
formula	$C_{66}H_{60}N_{14}O_{20}S_4Pr_2$	$C_{65}H_{56}N_{14}O_{19}S_4Nd_2$	$C_{66}H_{60}N_{14}O_{20}S_4Ho_2$	$C_{99}H_{113}N_{18}O_{46}S_9Cu_{18}$
fw	1779.34	1753.96	1827.38	3723.33
crystal system	Triclinic	Triclinic	Triclinic	Triclinic
crystal size, mm	0.24 × 0.22 × 0.22	0.20 × 0.18× 0.15	0.18 × 0.16 × 0.15	0.10 × 0.08 × 0.08
space group	P-1	P-1	P-1	P-1
a, Å	10.846(2)	11.081(2)	10.865(2)	14.9022(17)
b, Å	13.732(3)	13.384(3)	13.541(3)	23.706(2)
c, Å	14.625(3)	14.003(3)	14.535(3)	24.274(3)
α, °	63.47(3)	64.73(3)	63.62(3)	77.651(3)
β, °	86.17(3)	77.09(3)	86.44(3)	87.562(4)
γ, °	70.77(3)	79.67(3)	70.70(3)	79.089(4)
V, $Å^3$	1831.8(6)	1822.2(7)	1798.9(6)	8225.5(16)
Dc, Mg m^{-3}	1.613	1.598	1.687	1.503
Z	1	1	1	2
μ, mm^{-1}	1.509	1.603	2.382	2.458
reflns collected/unique	23010 / 8715 [R(int) = 0.0338]	22787 / 8654 [R(int) = 0.0431]	10367 / 6992 [R(int) = 0.0225]	56644 / 28449 [R(int) = 0.0377]
data/restraints/parameters	8715 / 0 / 472	8654 / 0 / 473	6992 / 1 / 496	28449 / 168 / 1718
R^a	0.0426	0.0537	0.0315	0.0638
$R_w{}^b$	0.0932	0.1455	0.0462	0.1712
GOF on F^2	1.123	1.022	1.005	1.042
$\Delta\rho_{min}$ and $\Delta\rho_{max}$, e $Å^{-3}$	-0.964 and 0.620	-1.262 and 1.170	-0.557 and 0.637	-1.601 and 2.374

Table S2 Metal ion analyses for compounds **2, 3** and **4**

Sample	ICP	EDS
Polymer **2**	---	---
Polymer **3**	Cu 89.5% Zn 10.5%	Cu 90.4% Zn 9.6%
Polymer **4**	Cu 84.4% Co 15.6%	Cu 85.50% Co14.50%