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Supplementary Material

A novel (3,4,9)-connected 3-D metal-organic framework based on the non-planar tricarboxyl tecton and Zn_5O_4 -cluster SBU

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Experimental Section

X-ray Data Collection and Structure Determination on **1**

X-Ray single-crystal diffraction data for **1** was collected on a Bruker Smart 1000 CCD area-detector diffractometer at 293(2) K with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) by ω scan mode. The program SAINT (Bruker AXS, *SAINT Software Reference Manual*, Madison: WI, **1998**) was used for integration of the diffraction profiles and a semi-empirical absorption correction was applied using the SADABS program (G. M. Sheldrick, *SADABS, Siemens Area Detector Absorption Corrected Software*, University of Göttingen: Germany, **1996**). All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL (G. M. Sheldrick, *SHELXTL NT Version 5.1. Program for Solution and Refinement of Crystal Structures*, University of Göttingen: Germany, **1997**). Metal ions in all the complexes were located from the E -maps, and the other non-H atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2 . Hydrogen atoms were generated theoretically and refined with isotropic thermal parameters riding on the parent atoms. In this structure, Zn2, O8, O11, O15, and O17 were treated with the similar disordered models of 0.62/0.38 occupancy.

Table S1 Crystallographic data and structure refinement summary for **1**.^a

Compound reference	1
Chemical formula	C ₄₂ H ₃₄ O ₂₀ Zn ₅
Formula Mass	1185.61
Crystal system	Monoclinic
<i>a</i> /Å	23.5728(14)
<i>b</i> /Å	6.4248(2)
<i>c</i> /Å	31.1276(15)
<i>α</i> /°	90.00
<i>β</i> /°	94.773(5)
<i>γ</i> /°	90.00
Unit cell volume/Å ³	4697.9(4)
Temperature/K	293(2)
Space group	<i>P</i> 2(1)/ <i>c</i>
No. of formula units per unit cell, <i>Z</i>	4
Absorption coefficient, μ/mm ⁻¹	2.587
No. of reflections measured	8271
No. of independent reflections	8271
<i>R</i> _{int}	0.0000
Final <i>R</i> _{<i>I</i>} values (<i>I</i> > 2σ(<i>I</i>))	0.0755
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2σ(<i>I</i>))	0.1588
Final <i>R</i> _{<i>I</i>} values (all data)	0.1587
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.1880
Goodness of fit on <i>F</i> ²	0.949

^a $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; ^b $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2 Selected bond lengths (Å) and angles (°) for **1**.^a

Zn2–O13	1.863(5)	Zn2–O15 ^{#1}	1.857(10)
Zn2–O8 ^{#2}	2.149(9)	Zn2–O16 ^{#1}	2.173(8)
Zn2–O9 ^{#3}	2.467(7)	Zn1–O2	1.915(6)
Zn1–O12 ^{#6}	1.935(6)	Zn1–O13	1.997(6)
Zn1–O7	2.030(6)	Zn3–O16	1.933(6)
Zn3–O5	1.975(8)	Zn3–O3 ^{#7}	1.970(7)
Zn3–O14	1.987(6)	Zn4–O6	1.941(9)
Zn4–O4 ^{#7}	2.053(8)	Zn4–O16 ^{#4}	2.063(5)
Zn4–O14	2.068(6)	Zn4–O18	2.205(2)
Zn4–O9	2.151(7)	Zn5–O10	1.999(6)
Zn5–O13 ^{#8}	2.010(5)	Zn5–O14	2.079(6)
O13–Zn2–O15 ^{#1}	123.8(4)	O13–Zn2–O8 ^{#2}	83.9(3)
O15 ^{#1} –Zn2–O8 ^{#2}	106.1(4)	O13–Zn2–O16 ^{#1}	119.0(3)
O15 ^{#1} –Zn2–O16 ^{#1}	115.3(4)	O8 ^{#2} –Zn2–O16 ^{#1}	93.8(3)
O13–Zn2–O9 ^{#3}	94.1(2)	O15 ^{#1} –Zn2–O9 ^{#3}	88.4(4)
O8 ^{#2} –Zn2–O9 ^{#3}	163.8(3)	O16 ^{#1} –Zn2–O9 ^{#3}	73.0(2)
O2–Zn1–O12 ^{#6}	116.0(3)	O2–Zn1–O13	129.3(3)
O12 ^{#6} –Zn1–O13	105.2(2)	O2–Zn1–O7	101.6(3)
O12 ^{#6} –Zn1–O7	114.7(3)	O13–Zn1–O7	85.8(2)
O16–Zn3–O5	107.5(3)	O16–Zn(3)–O3 ^{#7}	103.1(3)
O5–Zn3–O3 ^{#7}	111.9(3)	O16–Zn3–O14	124.2(3)
O5–Zn3–O14	109.5(3)	O3 ^{#7} –Zn3–O14	100.1(2)
O6–Zn4–O4 ^{#7}	100.4(3)	O6–Zn4–O16 ^{#4}	154.5(3)
O4 ^{#7} –Zn4–O16 ^{#4}	91.6(3)	O6–Zn4–O14	103.4(3)
O4 ^{#7} –Zn4–O14	92.7(3)	O16 ^{#4} –Zn4–O14	98.4(2)
O6–Zn4–O18	61.6(8)	O4 ^{#7} –Zn4–O18	77.0(8)
O16 ^{#4} –Zn4–O18	100.1(7)	O14–Zn4–O18	159.1(7)
O6–Zn4–O9	84.3(3)	O4 ^{#7} –Zn4–O9	173.1(3)
O16 ^{#4} –Zn4–O9	82.1(3)	O14–Zn4–O9	91.1(2)
O18–Zn4–O9	101.1(7)	O15–Zn5–O10	92.2(4)
O15–Zn5–O13 ^{#8}	157.4(4)	O10–Zn5–O13 ^{#8}	104.2(2)
O15–Zn5–O14	103.8(4)	O10–Zn5–O14	97.6(3)
O13 ^{#8} –Zn5–O14	89.6(2)	O15–Zn5–O17	64.8(6)

O10–Zn5–O17

100.8(5)

O13^{#8}–Zn5–O17

96.4(5)

O14–Zn5–O17

158.6(5)

Symmetry codes for **1**: #1 = $x, -y + 3/2, z + 1/2$; #2 = $x, y + 1, z$; #3 = $x, -y + 1/2, z + 1/2$; #4 = $x, y - 1, z$; #5 = $x, -y + 3/2, z - 1/2$; #6 = $-x + 1, -y + 1, -z + 1$; #7 = $-x, y - 1/2, -z + 1/2$; #8 = $x, -y + 1/2, z - 1/2$; #9 = $-x, y + 1/2, -z + 1/2$.

PXRD pattern

To confirm whether the crystal structures are truly representative of the bulk materials, powder X-ray diffraction (PXRD) experiment was carried out for **1**. Simulation of the PXRD spectra was carried out by the single-crystal data and diffraction-crystal module of the *Mercury* (Hg) program available free of charge via the Internet at <http://www.iucr.org>. The PXRD experimental and computer-simulated pattern is shown in Fig. S1. Although the experimental pattern shows a few unindexed diffraction lines and some diffraction lines are slightly broadened in comparison with those simulated from the single crystal modes, it still can be considered favorably that the bulk synthesized materials and the as-grown crystals are homogeneous for **1**.

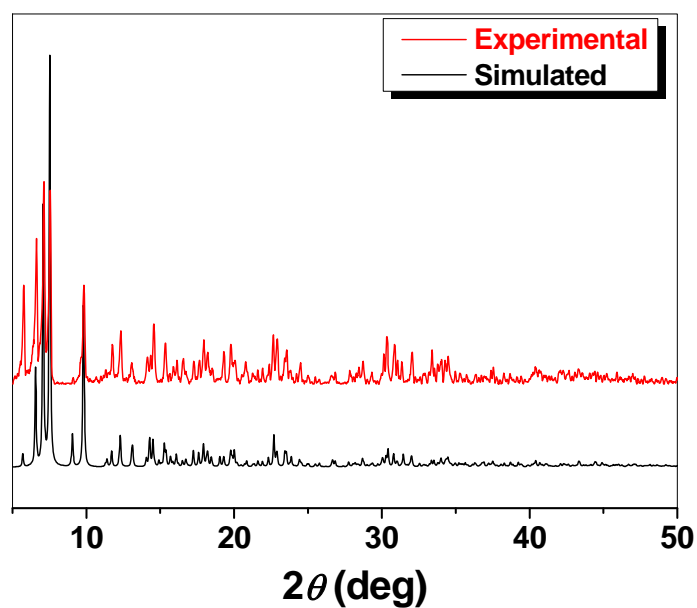


Fig. S1. PXRD pattern of **1**.

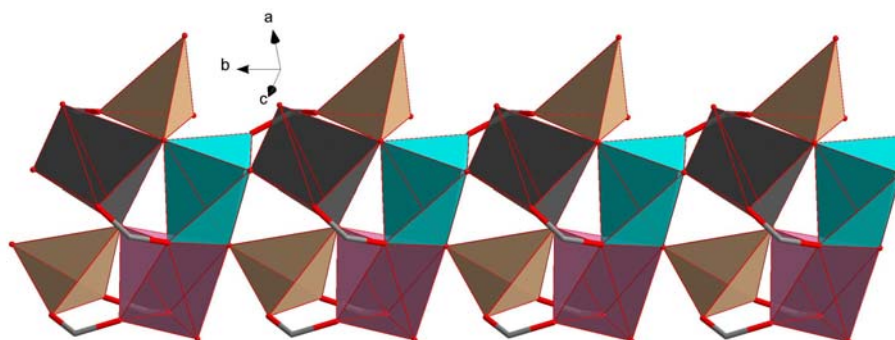
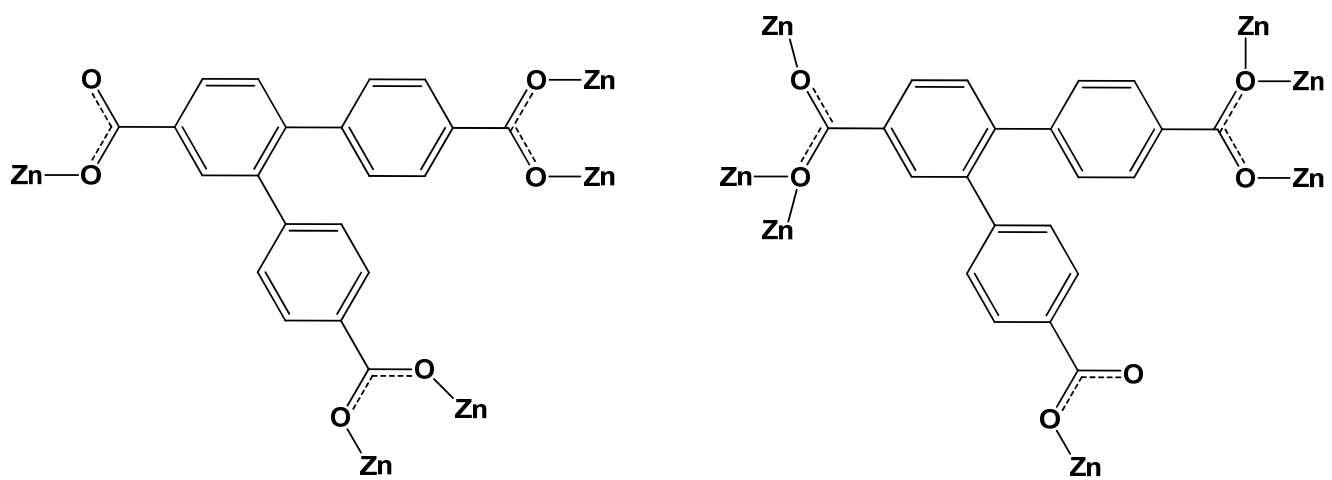


Fig. S2. View of the 1-D polymeric chain motif along the *b* axis with the pentanuclear Zn(II) SBUs, featuring the node-sharing overlap mode (tan tetrahedrons: Zn1 and Zn3; turquoise trigonal bipyramid: Zn2; rose octahedron: Zn4; grey square pyramid: Zn5).



Scheme S1. Coordination modes of fully deprotonated **L** ligand in **1**.

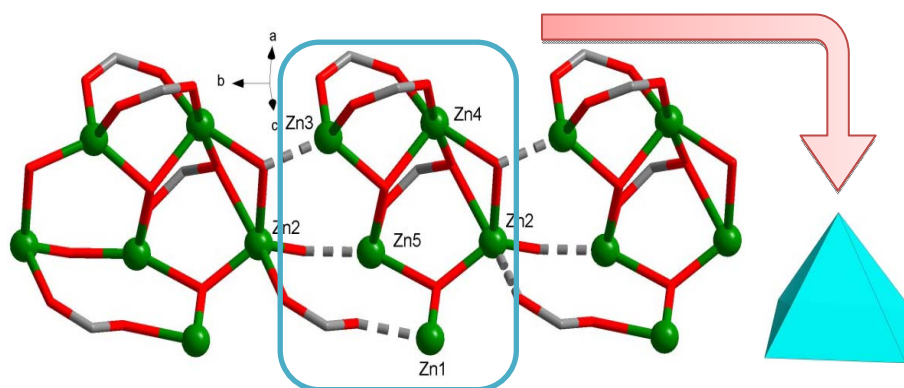


Fig. S3. View of the 1-D $[\text{Zn}_5(\mu_3\text{-OH})_3(\mu_2\text{-OH})]_n$ polymeric chain highlighting the pentanuclear motif as a cyan square pyramid model.

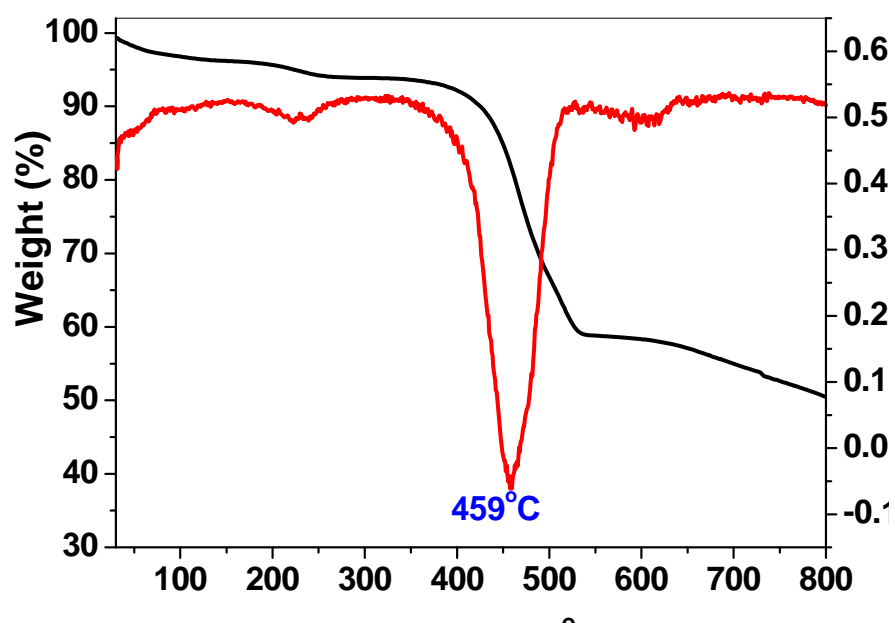


Fig. S4. TG-DTA curve of **1**.

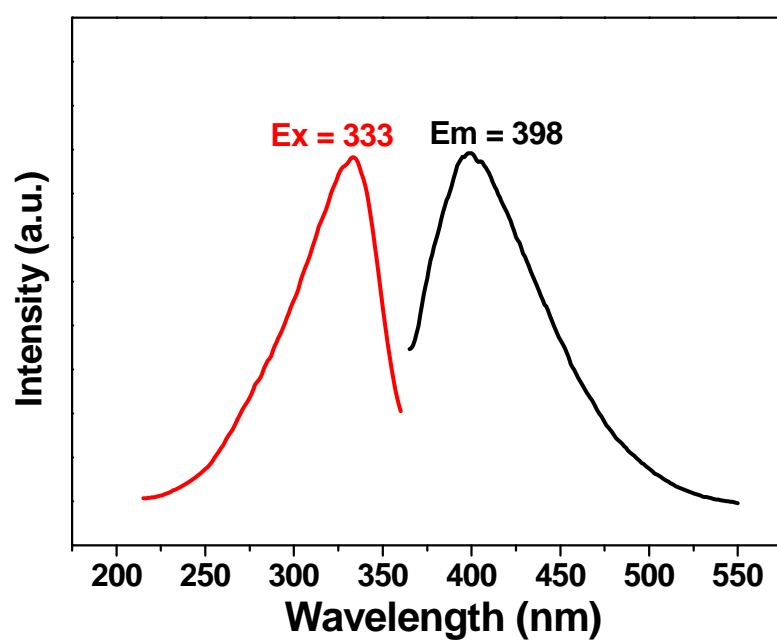


Fig. S5. Solid state excitation and emission spectra of H₃L ligand.