Electronic Supplementary Information

Unusual 3D Zn\textsuperscript{II} Coordination Networks with Mixed Tetrahedral and Square-Planar Building Units: From 2-Fold Interpenetrating bbf Architecture to Self-Penetrating 8\textsuperscript{6} Topological Framework

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Materials and General Methods

All the solvents and reagents for syntheses were commercially available and used as received. FT-IR spectra were recorded as KBr pellets on a Thermo Nicolet Nexus 670 FT-IR spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 Series II analyzer. Powder X-ray diffraction (PXRD) patterns were taken on a Rigaku D/max-2500 diffractometer (Cu Kα radiation, λ = 1.5406 Å), with a scan speed of 2 °/min and a step size of 0.02° in 2θ. The calculated PXRD patterns were simulated by using the single-crystal X-ray diffraction data. Thermogravimetric (TG) curves were recorded on a NETZSCH STA 449C microanalyzer in nitrogen atmosphere at a heating rate of 10 °C·min⁻¹. Solid-state fluorescent spectra were measured on a Perkin-Elmer LS50B luminescence spectrophotometer.

Single Crystal X-ray Crystallography

Single-crystal X-ray diffraction data for complexes 1 and 2 were collected on a Bruker APEX II CCD diffractometer with graphite monochromated Mo Ka radiation (0.71073 Å) at 291(2) K. Empirical absorption corrections were applied using the SADABS program.¹ The structures were solved by direct methods and refined based on $F^2$ by the full matrix least-squares methods using SHELXTL.² ³ All non-H atoms were refined anisotropically. The H atoms were located geometrically and refined as riding. Selected bond geometries for 1 and 2 are listed in Table S1.

References

1 Sheldrick, G M. SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, 1997.
2 Sheldrick, G. M. SHELXS-97, Program for the Solution of Crystal Structures; University of Göttingen, Germany, 1997.
Table S1 Selected Bond Distances (Å) and Angles (deg) for 1 and 2

<table>
<thead>
<tr>
<th></th>
<th>1a</th>
<th>2b</th>
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<tr>
<td>Zn1-O1</td>
<td>1.911(4)</td>
<td>Zn1-N2</td>
</tr>
<tr>
<td>Zn1-O3#1</td>
<td>1.950(4)</td>
<td>Zn1-N5#2</td>
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<td>122.44(2)</td>
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<td>100.79(2)</td>
<td>O3#1-Zn1-N5#2</td>
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<td>O3#1-Zn1-N2</td>
<td>106.73(2)</td>
<td>N2-Zn1-N5#2</td>
</tr>
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a Symmetry codes for 1: #1 = -0.5 + x, 0.5 - y, -0.5 + z; #2 = -0.5 - x, -0.5 + y, 0.5 - z.

b Symmetry codes for 2: #1 = 0.5 + x, 1.5 - y, 0.5 + z.

Figure S1. The left- and right-hand helical pillars constructed from Zn$^{II}$ centers and bip ligands.
**Figure S2.** Different self-catenated patterns consisting of five types of 8-membered circuits analyzed by TOPOS program. Five types of 8-membered circuits are shown as following: Circuit no 1, type=8a, centroid: (0.500,0.500,0.500); Circuit no 2, type=8b, centroid: (0.091,0.293,0.915); Circuit no 3, type=8c, centroid: (0.596,0.769,0.398); Circuit no 4, type=8d, centroid: (0.500,0.500,0.000); Circuit no 5, type=8e, centroid: (0.500,0.500,0.500).
Figure S3. PXRD patterns for (a) 1 and (b) 2.
Figure S4. TG curve of 1

Figure S5. TG curve of 2.

Figure S6. Emission spectra of 1 (pink) and 2 (green) in solid state at room temperature