

< **Electronic Supplementary Information** >

**An Interwoven Fe₃L₃ Trigonal Metallamacrocycle from *in situ*
Ligand-Disassembly Reaction**

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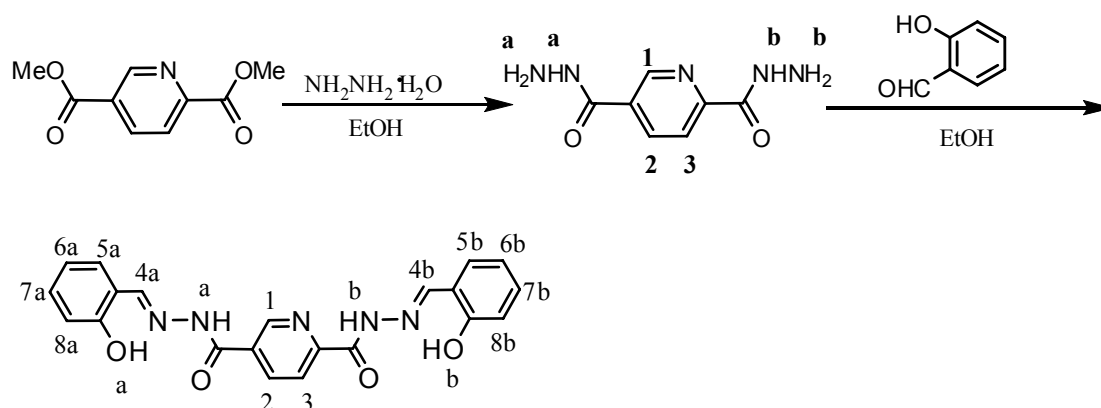
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Experiment Section

Materials and methods. All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. Elemental analyses were carried out by the Elemental Analysis Lab of our Institute. The FT-IR spectra were recorded as KBr pellets on a PerkinElmer Spectrum One FT-IR spectrometer. Thermal gravimetric (TG) analyses were performed with heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under on a NETZSCH STA 449C simultaneous TG-DSC instrument. ^1H NMR spectra were measured on a Varian INOVA 400M spectrometer. ESI-MS spectra were recorded on Finnigan DECAX-30000 LCQ Deca XP ion trap mass spectrometer. Magnetic measurement was carried out with a Quantum Design PPMS model 6000 magnetometer.

1.1 Synthesis of the ligand $\text{H}_4\text{L1}$



Scheme S1. Synthesis of the bishydrazone ligand $\text{H}_4\text{L1}$.

Pyridine-2,5-dicarbohydrazide: A mixture solution of 80% hydrazine hydrate (1.25 g, 20 mmol) and dimethyl pyridine-2,5-dicarboxylate (1.95 g, 10 mmol) in ethanol (50mL) was stirred over 10 h. The white precipitate formed, was collected by filtration, washed with ethanol and dried *in vacuo*. Yield: (1.76 g, 90%). Elemental analysis calcd (%) for $\text{C}_7\text{H}_9\text{N}_3\text{O}_2$: C 43.08, H 4.65, N 35.88; found: C 43.05, H 4.63; N 35.91. ^1H NMR (400 MHz, $\text{DMSO-}d_6$, ppm): 10.097 (br, 1H, $-\text{NH}_b$), 10.057 (br, 1H, $-\text{NH}_a$), 8.971 (1H, H_1), 8.332 (d, 1H, $J = 8\text{ Hz}$, H_2), 8.065 (d, 1H, $J = 8\text{ Hz}$, H_3), 4.617 (4H, $-\text{NH}_2$). ESI-MS: $m/z = 196.3$ [$\text{M}+\text{H}^+$].

$\text{H}_4\text{L1}$: Pyridine-2,5-dicarbohydrazide (2.00 g, 10mmol) and salicylaldehyde (2.5 g,

10 mmol) were refluxed for 8 h under nitrogen in ethanol (40 ml) with addition 3 drops of acetic acid. During the reaction, a pale yellow precipitate was formed, which was collected by filtration, washed with ethanol and diethyl ether three times, respectively, and dried *in vacuo*. Yield: 3.60 g, 89%. Elemental analysis calcd (%) for C₂₁H₁₇N₅O₄: C 62.53, H 4.25, N 17.36; found: C 62.48, H 4.20; N 17.42. ¹H NMR (400 MHz, DMSO-*d*₆, ppm): 12.653 (br, 1H, -NH_a), 12.397 (br, 1H, -NH_b), 11.345(br, 1H, -OH_a), 11.076 (br, 1H, -OH_b), 9.186 (s, 1H, H₁), 8.888(s, 1H, H_{4a}), 8.697 (s, 1H, H_{4b}), 8.529 (d, 1H, *J* = 6 Hz, H₂), 8.305 (d, 1H, *J* = 6 Hz, H₃), 7.625 (s, 1H, H_{5a}), 7.506 (s, 1H, H_{5b}), 7.331 (br, 2H, H_{7a}+H_{7b}), 6.947 (br, 4H, H_{6a}+H_{6b}+H_{8a}+H_{8b}). IR (KBr, cm⁻¹): 3431, 3223, 3085, 1642, 1605, 1486, 1462, 1365, 1314, 1203, 1150, 872, 760, 699. ESI-MS: *m/z* = 404.5 [H₄L1+H⁺].

1.2 Synthesis of the compound 1

The ligand H₄L1 (40 mg, 10 mmol) was added to a stirred solution of Fe(ClO₄)₃·6H₂O (46 mg, 10 mmol) in methanol (40 ml), and this mixture was continuously stirred for 4 h and then allowed to stand at room temperature after filtration. The black block crystals of **1** that were suitable for X-ray diffraction were obtained after several days. Yield: about 70% (based on the crystals that have been collected). Elemental analysis calcd (%) for C₄₂H₄₄N₉O₂₄Fe₃ (1226.40): C 41.13, H 3.62, N 10.28; found: C 41.20, H 3.55, N 10.32. IR (KBr, cm⁻¹): 3422(br, H₂O), 1624(m, C=N), 1603(s, C=N-N=C), 1563(s), 1343(s, CO₂), 1208(m, C-O), 898(w), 752(m), 614(m), 458(w).

Safety Note! *Although we experienced no problems in handling the perchlorate compound, they should be treated with great caution due to their potential for explosion.*

1.3 Crystallographic data collection and structural refinement for compound 1

The diffraction data were measured with Mo K α radiation (λ = 0.71073 Å) on a Rigaku Mercury CCD diffractometer at 293(2) K. The SMART and SAINT program packages ¹ were used for data collection and integration, respectively. Collected data were corrected for absorbance using SADABS ² based upon Laue symmetry using

equivalent reflections. All structures were solved by direct methods and refined on F^2 by full-matrix least squares calculations with the using the SHELX-97 program package.³ All of the non-hydrogen atoms were refined with anisotropic thermal displacement coefficients. Hydrogen atoms on the disordered water molecules were not treated during the structural refinements, hydrogen atoms bound water molecules and amide groups were found in the difference maps, and the other hydrogen atoms of organic ligands were placed in the calculated positions. Crystallographic data and structure refinement for compound **1** are summarized in the Table S1.

References

- 1 SMART and SAINT, Area Detector Software Package and SAX Area Detector Integration Program; Bruker Analytical X-Ray; Madison, WI, USA, 1997.
- 2 SADABS, Area Detector Absorption Correction Program; Bruker Analytical X-Ray; Madison, WI, USA, 1997.
- 3 G. M. Sheldrick, SHELXTL. Version 5.1; Bruker Analytical X-ray Systems Inc.: Madison, WI, USA, 1997.

Table S1 Crystal Data and Structure Refinement Parameters for Compound **1**.

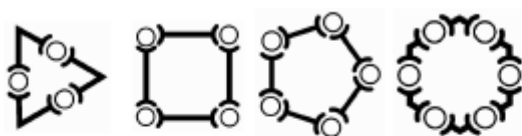
Compound	1
Formula	C ₄₂ H ₄₄ Fe ₃ N ₉ O ₂₄
FW	1226.40
Crystal system, Space group	Trigonal, <i>P</i> -3
<i>a</i> (Å)	17.5191 (15)
<i>b</i> (Å)	17.5191 (15)
<i>c</i> (Å)	12.0541 (17)
α (°)	90
β (°)	90
γ (°)	120
<i>V</i> (Å ³)	3204.0 (6)
<i>Z</i>	2
<i>D</i> _{calc} (Mg/m ³)	1.269
μ (mm ⁻¹)	0.745
Crystal size (mm)	0.25 x 0.20 x 0.10
Reflections collected / unique	19549 / 4850 [R(int) = 0.1012]
GOF	1.029
R1 (<i>I</i> > 2 σ (<i>I</i>)), wR2 (all data)	0.0572, 0.1451
Largest diff. peak and hole	0.812 and -0.520 Å ⁻³

Table S2 H-Bonding and $\pi \cdots \pi$ Stacking Interactions Parameters (Å, °) for Compound **1**.

	<i>D</i> —H (Å)	H \cdots <i>A</i> (Å)	<i>D</i> \cdots <i>A</i> (Å)	<i>D</i> —H \cdots <i>A</i> (°)
O5—H5A \cdots O6	0.83	1.79	2.607 (5)	164.6
O5—H5B \cdots O1 ⁱ	0.87	1.86	2.731 (3)	172.7
O6—H6A \cdots O7 ⁱⁱ	0.87	1.68	2.547 (9)	173.1
O6—H6B \cdots O6 ⁱⁱⁱ	1.00	1.91	2.871 (8)	160.4
O7—H7B \cdots O3	0.92	2.13	3.033 (6)	164.7
C4—H4 \cdots O3 ⁱⁱⁱ	0.93	2.52	3.429 (1)	165.3
Centroid-Centroid (Å) Interpalnar seperation (<i>h</i> , Å) Slip angle (θ , °)				
Cg1- Cg1 ⁱⁱ	3.834	3.680		16.29

Symmetry codes: (i) $y, -x+y, 1-z$; (ii) $1-x, -y, 1-z$; (iii) $-x+y, -x, z$.

(a) Coplanar



(b) Non-coplanar

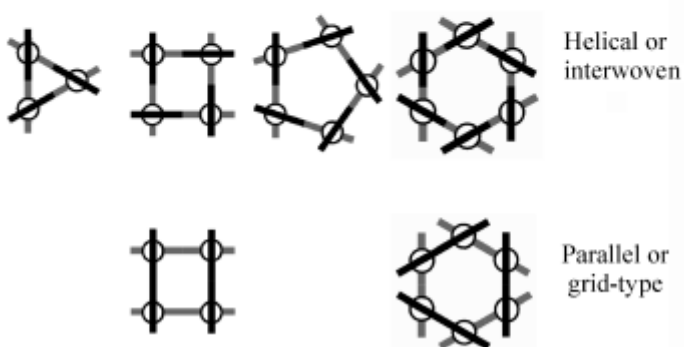


Fig. S1 Schematic diagrams for coplanar and non-coplanar polygonal metallamacrocycles.

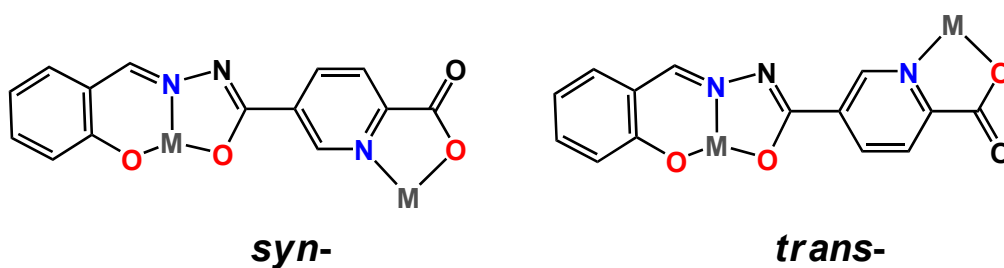


Fig. S2 The ligand L^{3-} with *cis*- or *trans*- conformations coordinated to the octahedral metal centers.

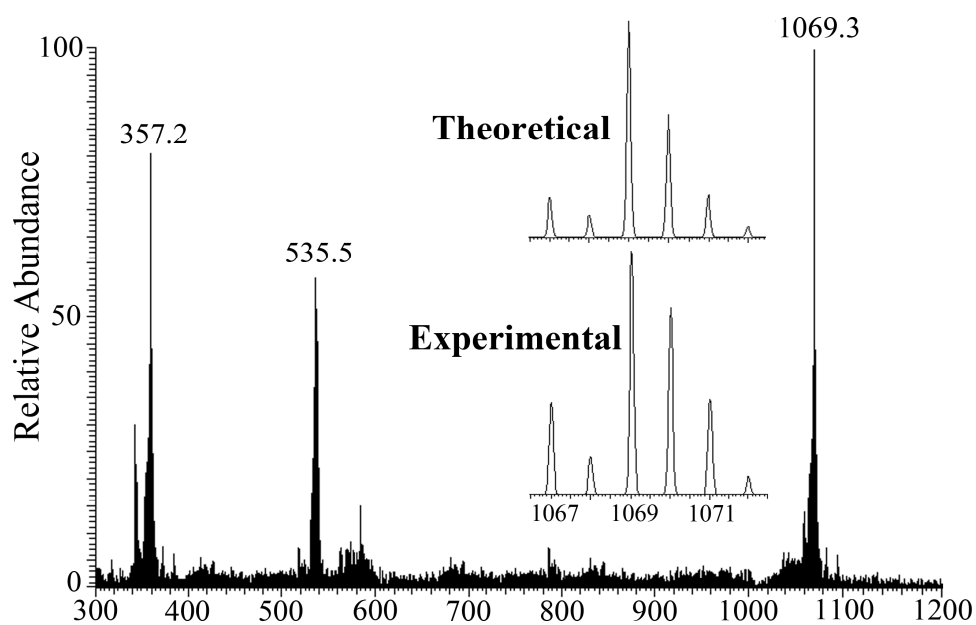


Fig. S3 ESI-MS spectrum for compound **1** in MeOH/DMF (2:1). The inset showing isotopic distribution patterns for measured and simulated isotopic patterns at m/z 1069.3.

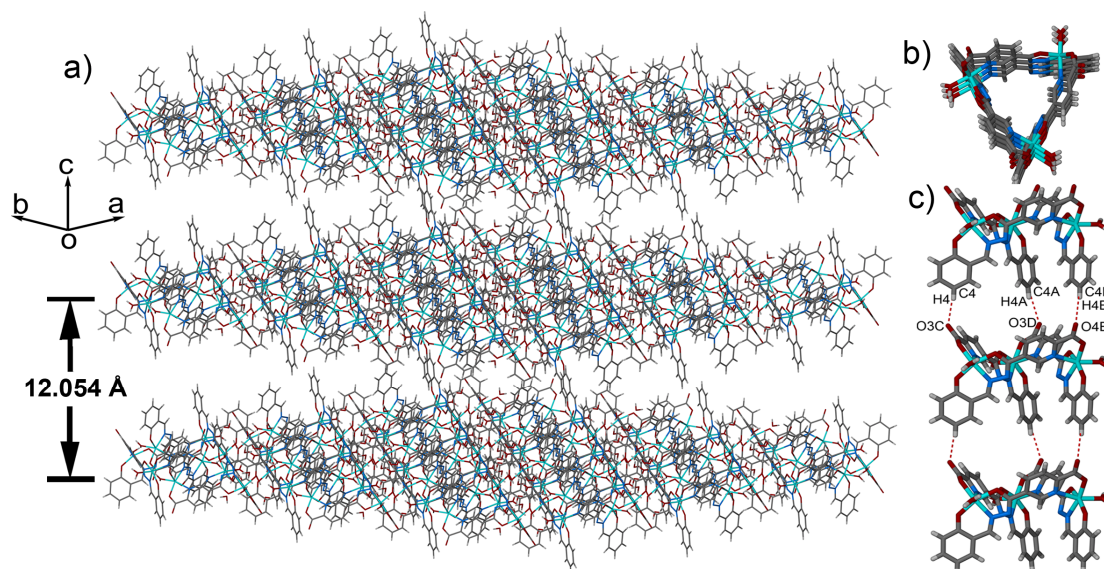


Fig. S4 a) Packing diagram of compound **1**; and b) top view and c) side view of the trigonal tube established through intermolecular C-H...O H-bonding interactions along *c* axis.

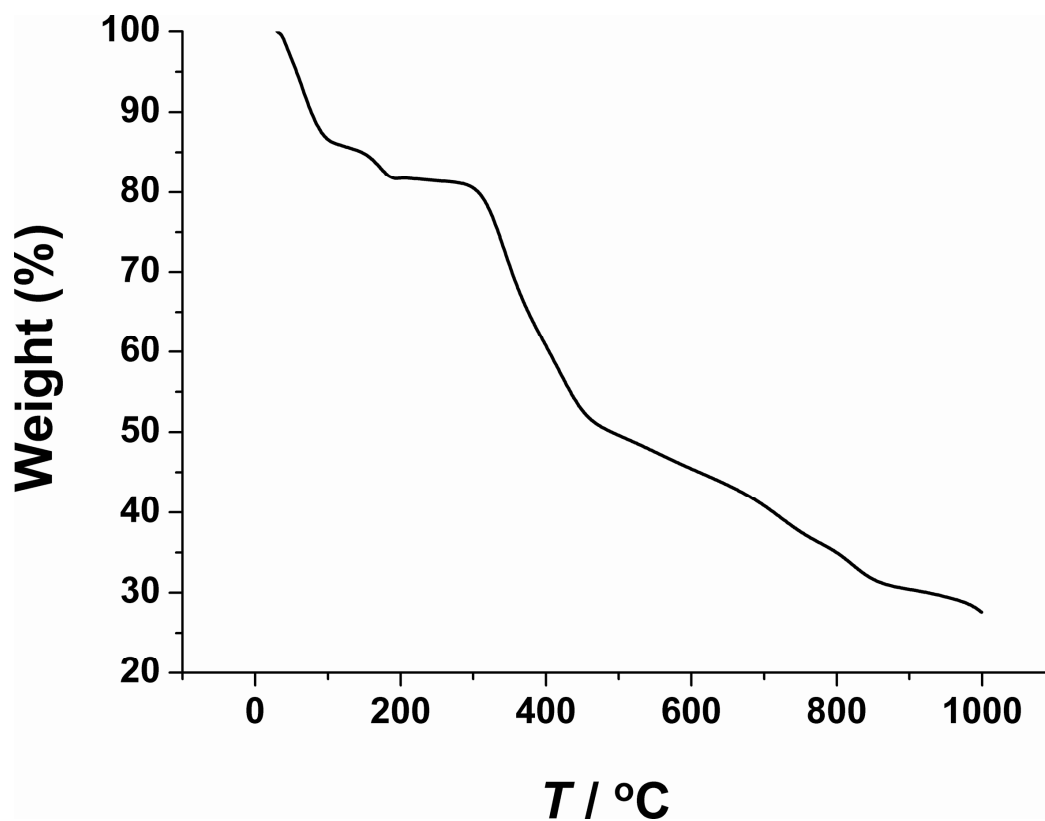


Fig. S5 The TGA curve for compound 1 in the temperature range 30-1000 °C under N₂ atmosphere.