Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Bottom-up Synthesis Strategy of Two-dimensional {Fe_5} Cluster-Based Coordination Polymer：Stepwise Formation of {Fe_5} Cluster and Its Dimension Augmentation

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Experimental

Materials and methods

Except for the ligands which were prepared according to the literature procedure,[1] the other chemicals were commercial products and were used without any further purification. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 2400II elemental analyzer. The Fourier transform infrared data were obtained on a Perkin-Elmer Spectrum One FT-IR spectrometer. Powder X-ray diffraction was measured on a Rigaku D/max diffractometer equipped (Cu-Kα, λ = 1.54056 Å). XPS spectra were measured by Electron spectrometer ESCALAB 250Xi. A FEI Quanta 200 scanning electron microscope (SEM) was used to determine the morphology. HRESI-MS measurements were conducted on a Thermo Exactive instrument at a capillary temperature of 275 K. A liquots of the solution were injected into the device at 0.3 mL/h. And the data were collected in positive ion mode. The spectrometer had previously been calibrated with standard tune mix to give a precision of about 2 ppm in the region of m/z 300-2000; the tube lens voltage was set at 150 V and the skimmer voltage at 25 V. The in-source energy was set to a range of 0-100 eV with a gas flow rate at 10% of the maximum.

Synthesis of $[Fe^{III}_4Fe^{II}O_2Cl_4(Hdpbt)_4]\cdot[Fe^{III}Cl_4]_2\cdot 4.5MeOH$ ({Fe_5}-0D).

A mixture of H_2dpbt (0.30 mmol, 0.0912 g), $FeCl_3\cdot 6H_2O$ (1 mmol, 0.2703 g) were added in 10 mL MeOH/2-butanol (V:V=9:1). The mixture was stirred at room temperature for 20min. The resulting reaction mixture was sealed in a Teflon-lined stainless steel vessel (25 mL) and maintained at 100 ℃ for 24h at 10 ℃/h. Brown-black block crystals were obtained. they were picked out, washed with ethanol, and dried in air (yield ca. 57% based on Fe^{III}). Anal. Calcd for $C_{56}H_{44}Cl_{13}Fe_7N_{32}O_6$: C, 30.39; H, 2.00; N, 20.25. Found: C, 35.22; H, 2.06; N, 20.33. IR (KBr, cm^{-1}): 3405(s), 3093(w), 2841(m), 2692(w), 1611(w), 1567(m), 1460(w), 1422(w), 1396(m), 1309(s), 1287(s), 1182(w), 1158(w), 1097(w), 1072(w), 1054(m), 1034(w), 1015(m), 1004(w), 979(w), 795(w), 751(w), 718(s), 686(s), 639(m), 634(m), 496(m).

Synthesis of $\{[Fe^{III}_4Fe^{II}_2O_2Cl_5(dpbt)_2(Hdpbt)_2]\cdot(Fe^{III}Cl_4)\cdot 6MeOH\}_n$ ({Fe_5}-1D)

Method 1. As-synthesized **{Fe_5}-0D** (ca. 25 mg of single crystals), $FeCl_3\cdot 6H_2O$ (0.054 g, 0.2 mmol) were added in a 5 mL MeOH/2-butanol (V:V=9:1) solution were stirred (10 min) in a Teflon-lined stainless steel vessel and placed under autogenous pressure at 170 ℃ for 24h. Brown-black strip crystals were obtained. Anal. Calcd for $C_{56}H_{38}Cl_9Fe_7N_{32}O_5$: C, 35.51; H, 1.97; N, 23.00. Found: C, 35.83; H, 1.98; N, 22.81. IR (KBr, cm^{-1}): 3405(s), 3093(s), 2841(s), 2692(m), 1611(s), 1567(m), 1460(s), 1422(s), 1396(s), 1353(w), 1309(s),

1287(s), 1182(m), 1097(m), 1073(m), 1054(m), 1034(m), 1015(m), 1005(m), 979(m), 900(w), 795(s), 752(s), 719(s), 686(s), 639(m), 634(m), 497(w).

Method 2. As-synthesized **{Fe_5}-0D** (ca. 25 mg of single crystals), $FeCl_3 \cdot 6H_2O$ (0.054 g, 0.2 mmol), and triethylamine (0.2ml) were added in a 5 mL MeOH/2-butanol (V:V=9:1) solution were stirred (10 min) in a Teflon-lined stainless steel vessel and placed under autogenous pressure at 100 ℃ for 24h.

Synthesis of {[$Fe^{III}_4Fe^{II}_3O_2Cl_5(dpbt)_4(H_2O)_{1.5}(MEK)_{0.5}]\cdot(Fe^{III}Cl_4)\cdot 8.5MeOH\}_n$ ({Fe_5}-2D)

Method 1. As-synthesized {Fe5}-0D (ca. 25 mg of single crystals) and $FeCl_3 \cdot 6H_2O$ (0.054 g, 0.2 mmol) in a 5 mL MeOH/2-butanol (V:V=9:1) solution were stirred (10 min) in a Teflon-lined stainless steel vessel and placed under autogenous pressure at 170 ℃ for 24h. The resulting black block crystals of **{Fe_5}-2D** in a yield of about 21% (based on **{Fe_5}-0D**) were obtained. Yield: 45% ◦ Anal. Calcd for $C_{55}H_{44}Cl_9Fe_8N_{32}O_{6.5}$: C, 33.83; H, 2.15; N, 21.77. Found: C, 34.02; H, 2.17; N, 21.59. IR (KBr, cm^{-1}): 3375(s), 1611(w), 1462(m), 1438(w), 1425(w), 1399(m), 1295(w), 1155(w), 1097(m), 1034(s), 1004(s), 794(w), 752(w), 722(w), 681(w), 631(m), 519(m).

Method 2. As-synthesized **{Fe_5}-0D** (ca. 25 mg of single crystals), $FeCl_3 \cdot 6H_2O$ (0.054 g, 0.2 mmol), and triethylamine (0.6ml) were added in a 5 mL MeOH/2-butanol (V:V=9:1) solution were stirred (10 min) in a Teflon-lined stainless steel vessel and placed under autogenous pressure at 100 ℃ for 24h.

X-ray crystallographic analysis

Single crystal X-ray diffraction data collection for **{Fe_5}-0D**, **{Fe_5}-1D** and **{Fe_5}-2D** were conducted on an Agilent Supernova diffractometer (Mo, λ = 0.71073Å) at room temperature. The crystal structures were solved using direct methods with the SHELXL program[2, 3] and refined with a full-matrix least-squares technique within the ShelXL and OLEX2.[4] All the non-hydrogen atoms were refined anisotropically. All H atoms were refined isotropically. Since the solvent molecules in the complex were obviously disordered, they could not be modeled correctly. Thus, the Solvent Mask procedure implemented in OLEX2 software was employed to calculate the diffraction contribution of the solvent molecules and thereby produce a set of solvent-free diffraction intensities. The Mask results for the complexes are provided in the Supporting Information. The crystallographic and refinement details are presented in **Table S5**. Selected bond lengths and bond angle are given in **Table S6.** CCDC reference numbers: 2112792-2112794.†

References:

1. F. P. Huang, P. F. Yao, H. Y. Li, Q. Yu, H. D. Bian and H. Liang, *Chem Commun*, 2015, **51**, 7598-7601.
2. G. M. Sheldrick, *Acta Crystallogr A*, 2008, **64**, 112-122.
3. G. M. Sheldrick, *Acta Crystallogr C Struct Chem*, 2015, **71**, 3-8.
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Journal of Applied Crystallography*, 2009, **42**, 339-341.

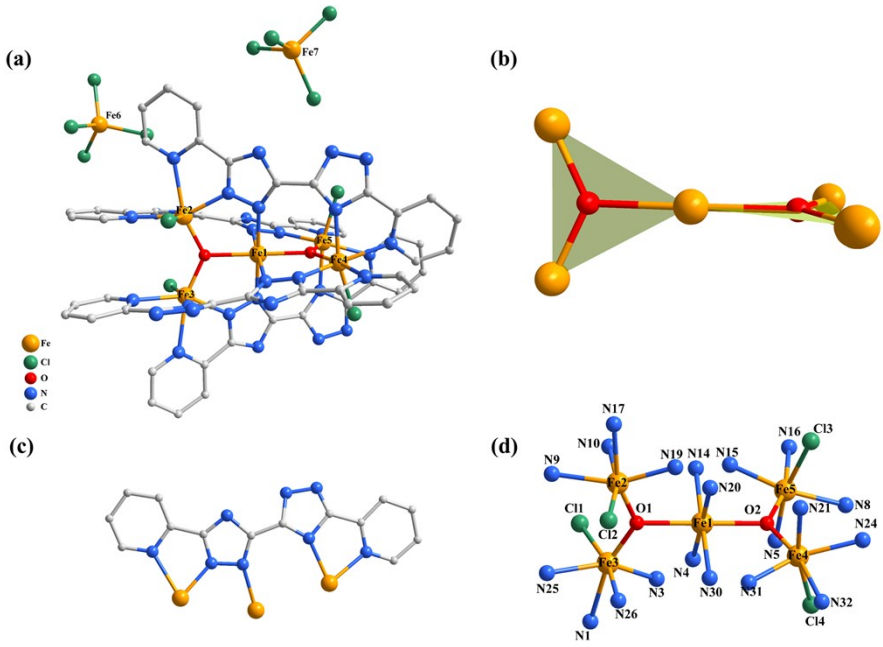


Fig. S1 The structure and [Fe_5] core of {**Fe_5}-0D** (a, b). Coordination mode of $Hdpbt^-$ ligand (c). Coordination environments of five crystallographically independent Fe ions in **{Fe_5}-0D** (d).

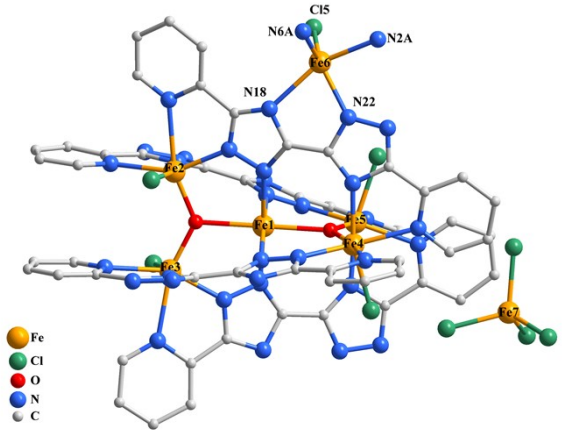


Fig. S2 Coordination environments of Fe ions in **{Fe_5}-1D.**

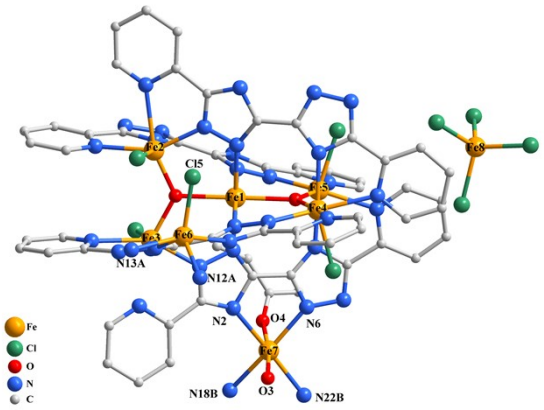


Fig. S3 Coordination environments of Fe ions in **{Fe$_5$}-2D.**

Table S1. SHAPE analysis of the Fe ions in {**Fe$_5$**}-0D, {**Fe$_5$**}-1D and {**Fe$_5$**}-2D

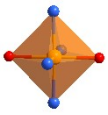
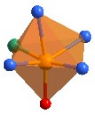
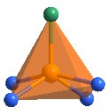
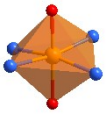
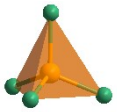
		FeN_4O_2	FeN_4OCl	FeN_4Cl	FeN_4O_2	$FeCl_4$
Coordination modes						
label symmetry shape		OC-6 Oh Octahedron	OC-6 Oh Octahedron	TBPY-5 D3h Trigonal bipyramid	OC-6 Oh Octahedron	T-4 Td Tetrahedron
Calculation results		distortion(τ_{min})				
Serial number	**{Fe$_5$}-0D**	Fe1 (0.022)	Fe2 (2.482), Fe3 (2.467), Fe4 (2.529), Fe5 (2.559)	-	-	Fe6 (0.005), Fe7 (0.026)
	{Fe$_5$}-1D	Fe1(0.085)	Fe2 (2.908), Fe3 (2.321), Fe4 (2.223), Fe5 (2.620)	Fe6 (2.523)	-	Fe7 (0.031)
	{Fe$_5$}-2D	Fe1 (0.007)	Fe2 (2.475), Fe3 (2.740), Fe4 (2.514), Fe5 (2.458)	Fe6 (2.154)	Fe7 (2.098)	Fe8(0.034)

Table S2. Bond Valence Sum (BVS)[a] , Calculations for Fe Atoms in **{Fe5}-0D, {Fe5}-1D** and **{Fe5}-2D.**

Complex	**{Fe5}-0D**		**{Fe5}-1D**		**{Fe5}-2D**	
Atom	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)
Fe1	**1.84**	2.048	**1.883**	2.100	**1.948**	2.168
Fe2	2.594	**2.866**	2.551	**2.816**	2.563	**2.831**
Fe3	2.459	**2.716**	2.616	**2.888**	2.567	**2.836**
Fe4	2.571	**2.839**	2.557	**2.826**	2.571	**2.841**

Fe5	2.527	**2.792**	2.621	**2.895**	2.579	**2.850**
Fe6	2.884	**3.128**	**2.037**	2.277	**1.923**	2.149
Fe7	2.879	**3.122**	2.933	**3.181**	**1.893**	2.323
Fe8					3.084	**3.345**

[a] The underlined value is the one closest to the charge for which it was calculated. The oxidation state is the nearest whole number to the underlined value

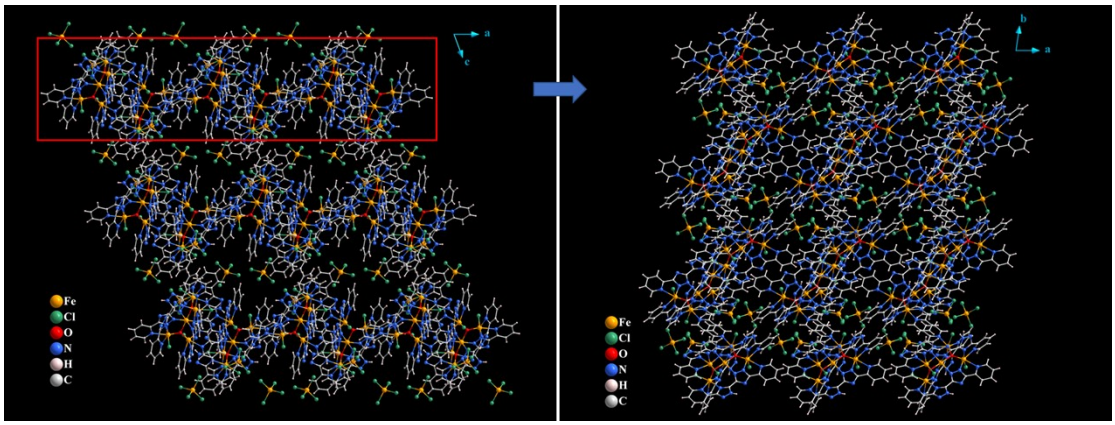


Fig. S4 The packing arrangement of **{Fe_5}-0D** along the b-axis and c-axis respectively.

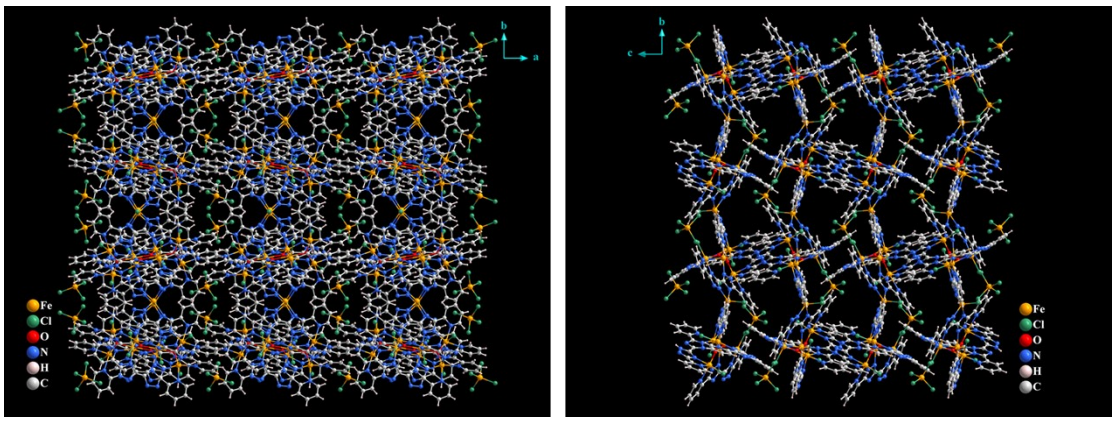


Fig. S5 The packing arrangement of **{Fe_5}-1D** along the c-axis and a-axis respectively.

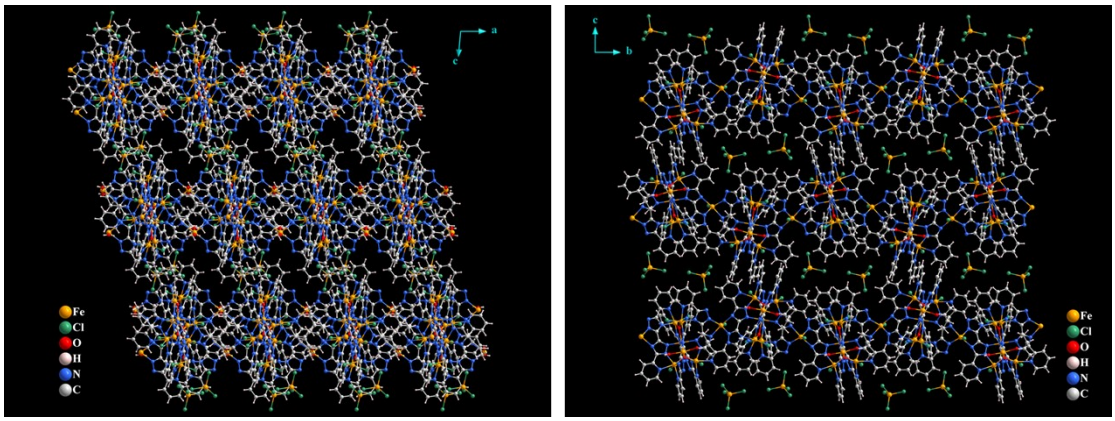


Fig. S6 The packing arrangement of **{Fe_5}-2D** along the b-axis and a-axis respectively.

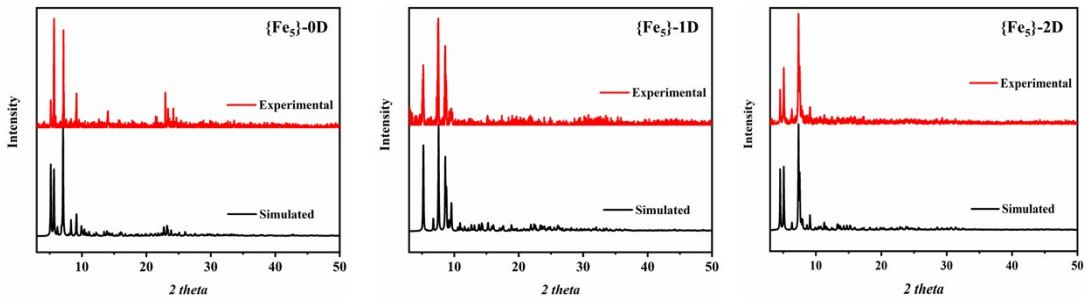


Fig. S7 Powdered X-ray diffraction (PXRD) patterns for **{Fe$_5$}-0D, {Fe$_5$}-1D** and **{Fe$_5$}-2D.**

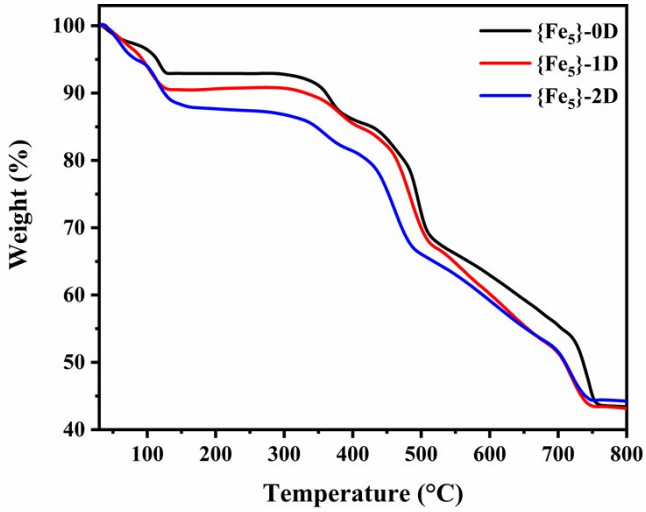
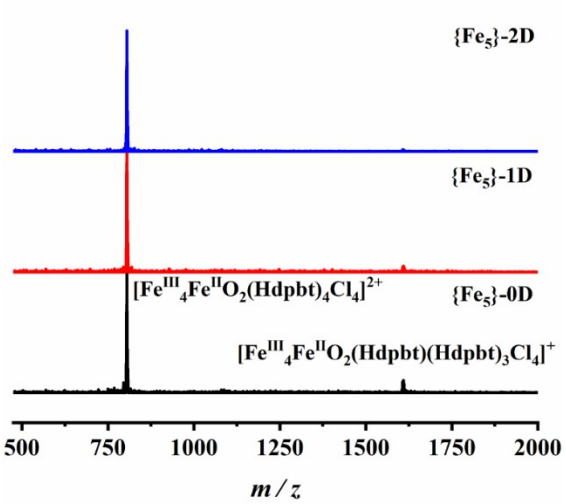


Fig. S8 The TGA plot of **{Fe$_5$}-0D, {Fe$_5$}-1D** and **{Fe$_5$}-2D**..



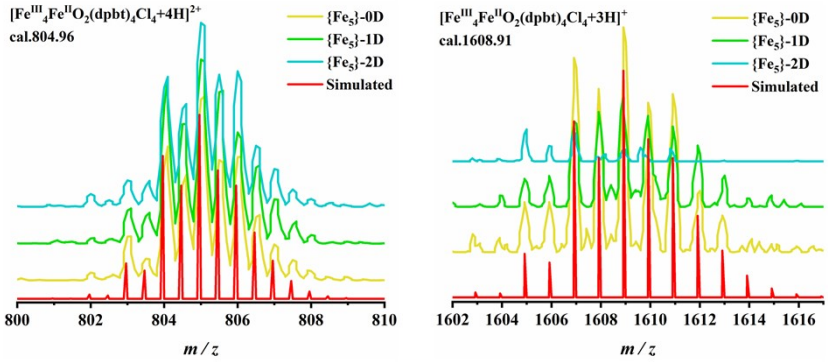


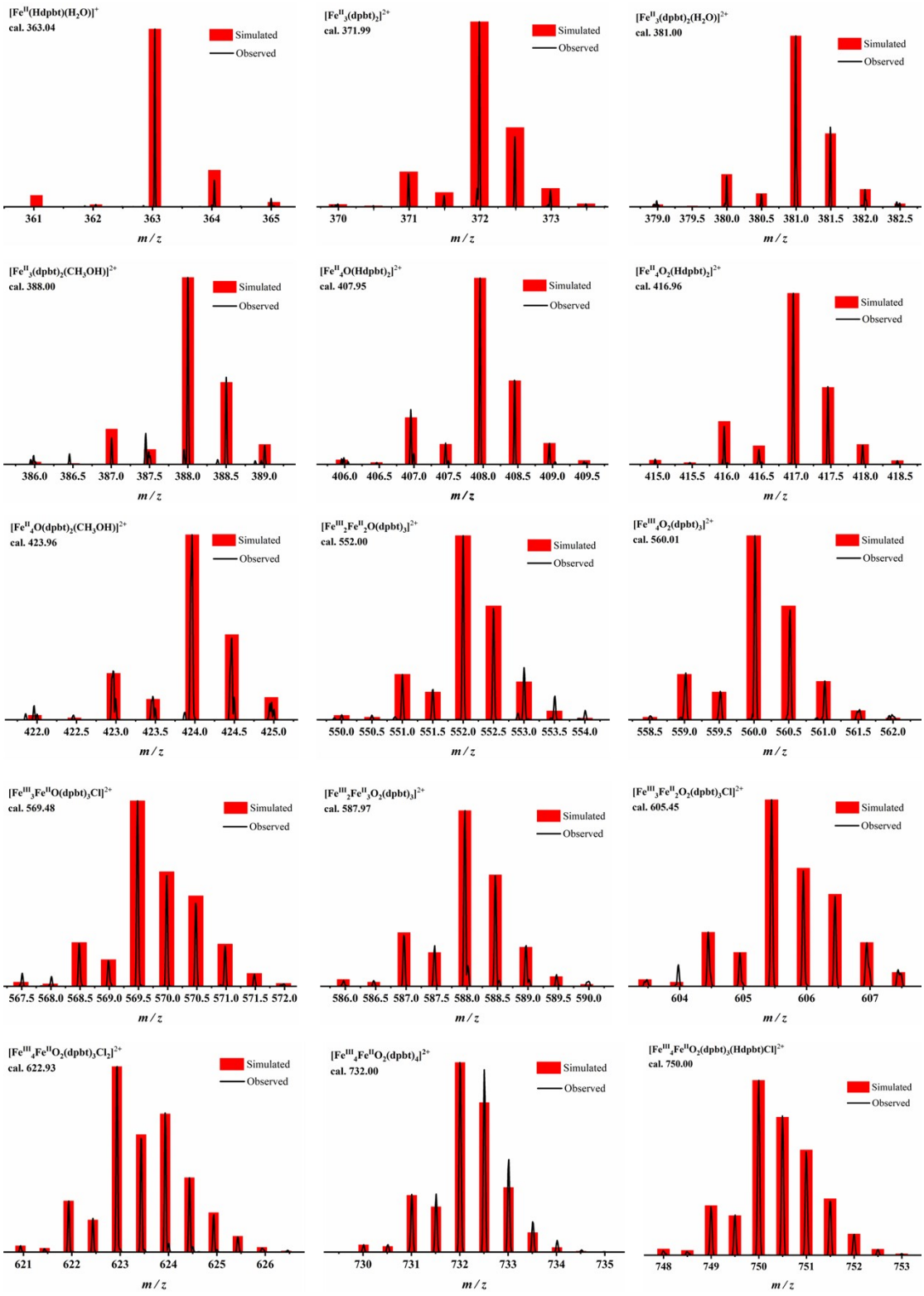
Fig. S9 Positive HRESI-MS spectra of **{Fe_5}-0D**, **{Fe_5}-1D**, and **{Fe_5}-2D** precursor in MeOH (In-Source CID = 0 eV) and schematic diagram of the {Fe_5} cluster structure.

Table S3. Major species assigned in the HRESI-MS in positive mode.

{Fe_5} (In-Source CID 0 eV)			
Peaks	Relative Intensity		
Typical Composition	Intensity	Observed *m/z*	Calculated *m/z*
$[Fe^{II}_3(dpbt)_2]^{2+}$	0.011	371.99	371.99
$[Fe^{II}_3(dpbt)_2(H_2O)]^{2+}$	0.051	381.00	381.00
$[Fe^{II}_4O_2(dpbt)_2+2H]^{2+}$	0.22	416.96	416.96
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl_4+4H]^{2+}$	1	804.96	804.96
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl_4+3H]^{+}$	0.0339	1608.91	1608.91
{Fe_5} (In-Source CID 40 eV)			
$[Fe^{II}_3(dpbt)_2]^{2+}$	0.021	371.99	371.99
$[Fe^{II}_3(dpbt)_2(H_2O)]^{2+}$	0.103	381.00	381.00
$[Fe^{II}_4O_2(dpbt)_2+2H]^{2+}$	1.14	416.96	416.96
$[Fe^{III}_3Fe^{II}O(dpbt)_3Cl]^{2+}$	0.129	569.48	569.48
$[Fe^{III}_4Fe^{II}O_2(dpbt)_3Cl_2]^{2+}$	0.123	622.93	622.93
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl+H]^{2+}$	0.191	750.00	750.00
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl_4+4H]^{2+}$	1	804.96	804.96
$[Fe^{III}_3Fe^{II}O(dpbt)_3Cl]^{+}$	0.0298	1138.96	1138.97
$[Fe^{III}_3Fe^{II}O_2(dpbt)_3Cl+H]^{+}$	0.0379	1155.96	1155.97
$[Fe^{III}_3Fe^{II}O(dpbt)_3Cl_2]^{+}$	0.0323	1173.94	1173.93
$[Fe^{III}_4Fe^{II}O_2(dpbt)_3Cl_3]^{+}$	0.0732	1280.83	1280.83
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl_4+3H]^{+}$	0.114	1608.91	1608.91
{Fe_5} (In-Source CID 60 eV)			
$[Fe^{II}(Hdpbt)(H_2O)]^{+}$	0.0521	363.04	363.04
$[Fe^{II}_3(dpbt)_2]^{2+}$	0.122	371.99	371.99
$[Fe^{II}_3(dpbt)_2(H_2O)]^{2+}$	0.219	381.00	381.00
$[Fe^{II}_3(dpbt)_2(CH_3OH)]^{2+}$	0.0223	388.00	388.00
$[Fe^{II}_4O(dpbt)_2]^{2+}$	0.0323	407.95	407.95
$[Fe^{II}_4O_2(dpbt)_2+2H]^{2+}$	0.113	416.96	416.96
$[Fe^{II}_4O(dpbt)_2(CH_3OH)]^{2+}$	0.0232	423.96	423.97

$[Fe^{III}_2Fe^{II}_2O(dpbt)_3]^{2+}$	0.108	552.00	552.00
$[Fe^{III}_4O_2(dpbt)_3]^{2+}$	0.0488	560.01	560.00
$[Fe^{III}_3Fe^{II}O(dpbt)_3Cl]^{2+}$	0.369	569.48	569.48
$[Fe^{III}_2Fe^{II}_3O_2(dpbt)_3]^{2+}$	0.0193	587.97	587.97
$[Fe^{III}_3Fe^{II}_2O_2(dpbt)_3Cl]^{2+}$	0.102	605.45	605.45
$[Fe^{III}_4Fe^{II}O_2(dpbt)_3Cl_2]^{2+}$	0.311	622.93	622.93
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4]^{2+}$	0.119	732.00	732.00
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl+H]^{2+}$	0.357	750.00	750.00
$[Fe^{III}_4Fe^{II}O(dpbt)_4Cl_2]^{2+}$	0.102	758.98	758.98
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl_2+2H]^{2+}$	0.0893	767.98	767.98
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl_4+4H]^{2+}$	1	804.96	804.96
$[Fe^{III}Fe^{II}_2(dpbt)_3]^{+}$	0.0687	1032.06	1032.07
$[Fe^{III}_3Fe^{II}O(dpbt)_3Cl]^{+}$	0.302	1138.96	1138.97
$[Fe^{III}_3Fe^{II}_2O_2(dpbt)_3Cl_2]^{+}$	0.134	1245.85	1245.86
$[Fe^{III}_4Fe^{II}O_2(dpbt)_3Cl_3]^{+}$	0.222	1280.83	1280.83
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl]^{+}$	0.0394	1498.97	1498.98
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl_2+H]^{+}$	0.0402	1534.96	1534.96
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl_3+2H]^{+}$	0.0193	1572.93	1572.93
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl_4+3H]^{+}$	0.134	1608.91	1608.91
$\{Fe_5\}$ (In-Source CID 80 eV)			
$[Fe^{II}(Hdpbt)(H_2O)]^{+}$	0.153	363.04	363.04
$[Fe^{II}_3(dpbt)_2]^{2+}$	0.462	371.99	371.99
$[Fe^{II}_3(dpbt)_2(H_2O)]^{2+}$	0.292	381.00	381.00
$[Fe^{II}_3(dpbt)_2(CH_3OH)]^{2+}$	0.0792	388.00	388.00
$[Fe^{II}_4O(dpbt)_2]^{2+}$	0.109	407.95	407.95
$[Fe^{II}_4O_2(dpbt)_2+2H]^{2+}$	0.362	416.96	416.96
$[Fe^{II}_4O(dpbt)_2(CH_3OH)]^{2+}$	0.0641	423.96	423.97
$[Fe^{III}_2Fe^{II}_2O(dpbt)_3]^{2+}$	0.237	552.00	552.00
$[Fe^{III}_4O_2(dpbt)_3]^{2+}$	0.0796	560.01	560.00
$[Fe^{III}_3Fe^{II}O(dpbt)_3Cl]^{2+}$	0.503	569.48	569.48
$[Fe^{III}_2Fe^{II}_3O_2(dpbt)_3]^{2+}$	0.0564	587.97	587.97
$[Fe^{III}_3Fe^{II}_2O_2(dpbt)_3Cl]^{2+}$	0.106	605.45	605.45
$[Fe^{III}_4Fe^{II}O_2(dpbt)_3Cl_2]^{2+}$	0.292	622.93	622.93
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4]^{2+}$	0.0504	732.00	732.00
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl+H]^{2+}$	0.193	750.00	750.00
$[Fe^{III}_4Fe^{II}O(dpbt)_4Cl_2]^{2+}$	0.0698	758.98	758.98
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl_2+2H]^{2+}$	0.0423	767.98	767.98
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl_4+4H]^{2+}$	0.544	804.96	804.96
$[Fe^{III}Fe^{II}_2(dpbt)_3]^{+}$	0.233	1032.06	1032.07
$[Fe^{III}_2Fe^{II}_2O(dpbt)_3Cl]^{+}$	1	1138.96	1138.97
$[Fe^{III}_3Fe^{II}O_2(dpbt)_3(CH_3O)]^{+}$	0.0823	1151.02	1151.01
$[Fe^{III}_3Fe^{II}O_2(dpbt)_2(Hdpbt)Cl]^{+}$	0.283	1155.96	1155.97
$[Fe^{III}_3Fe^{II}O(dpbt)_3Cl_2]^{+}$	0.211	1173.94	1173.93

$[Fe^{III}_3Fe^{II}_2O_2(dpbt)_3Cl_2]^+$	0.328	1245.85	1245.86
$[Fe^{III}_4Fe^{II}O_2(dpbt)_3Cl_3]^+$	0.614	1280.83	1280.83
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl]^+$	0.0606	1498.97	1498.98
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl_2+H]^+$	0.0721	1534.96	1534.96
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl_3+2H]^+$	0.0413	1572.93	1572.93
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl_4+3H]^+$	0.0347	1608.91	1608.91
{Fe_5} (In-Source CID 100 eV)			
$[Fe^{II}(Hdpbt)(H_2O)]^+$	0.217	363.04	363.04
$[Fe^{II}_3(dpbt)_2]^{2+}$	1	371.99	371.99
$[Fe^{II}_3(dpbt)_2(H_2O)]^{2+}$	0.423	381.00	381.00
$[Fe^{II}_3(dpbt)_2(CH_3OH)]^{2+}$	0.183	388.00	388.00
$[Fe^{II}_4O(dpbt)_2]^{2+}$	0.129	407.95	407.95
$[Fe^{II}_4O_2(dpbt)_2+2H]^{2+}$	0.417	416.96	416.96
$[Fe^{II}_4O(dpbt)_2\ (CH_3OH)]^{2+}$	0.0589	423.96	423.97
$[Fe^{III}_2Fe^{II}_2O(dpbt)_3]^{2+}$	0.362	552.00	552.00
$[Fe^{III}_4O_2(dpbt)_3]^{2+}$	0.139	560.01	560.00
$[Fe^{III}_3Fe^{II}O(dpbt)_3Cl]^{2+}$	0.501	569.48	569.48
$[Fe^{III}_2Fe^{II}_3O_2(dpbt)_3]^{2+}$	0.104	587.97	587.97
$[Fe^{III}_3Fe^{II}_2O_2(dpbt)_3Cl]^{2+}$	0.166	605.45	605.45
$[Fe^{III}_4Fe^{II}O_2(dpbt)_3Cl_2]^{2+}$	0.267	622.93	622.93
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4]^{2+}$	0.0815	732.00	732.00
$[Fe^{III}_4Fe^{II}(O)_2(dpbt)_4Cl+H]^{2+}$	0.119	750.00	750.00
$[Fe^{III}_4Fe^{II}O(dpbt)_4Cl_2]^{2+}$	0.0476	758.98	758.98
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl_2+2H]^{2+}$	0.0131	767.98	767.98
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl_4+4H]^{2+}$	0.104	804.96	804.96
$[Fe^{III}Fe^{II}_2(dpbt)_3]^+$	0.157	1032.06	1032.07
$[Fe^{III}_2Fe^{II}_2\ (O)(dpbt)_3Cl]^+$	0.579	1138.96	1138.97
$[Fe^{III}_3Fe^{II}O_2(dpbt)_3(CH_3O)]^+$	0.0467	1151.02	1151.01
$[Fe^{III}_3Fe^{II}O_2(dpbt)_3Cl+H]^+$	0.103	1155.96	1155.97
$[Fe^{III}_3Fe^{II}O(dpbt)_3Cl_2]^+$	0.0916	1173.94	1173.93
$[Fe^{III}_3Fe^{II}_2O_2(dpbt)_3Cl_2]^+$	0.223	1245.85	1245.86
$[Fe^{III}_4Fe^{II}O_2(dpbt)_3Cl_3]^+$	0.328	1280.83	1280.83
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl]^+$	0.175	1498.97	1498.98
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl_2+H]^+$	0.139	1534.96	1534.96
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl_3+2H]^+$	0.0697	1572.93	1572.93
$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl_4+3H]^+$	0.325	1608.91	1608.91


[Fe^II(Hdpbt)(H2O)]+
cal. 363.04
Simulated
Observed
361 362 363 364 365
m/z
[Fe^II3(dpbt)2]2+
cal. 371.99
Simulated
Observed
370 371 372 373
m/z
[Fe^II3(dpbt)2(H2O)]2+
cal. 381.00
Simulated
Observed
379.0 379.5 380.0 380.5 381.0 381.5 382.0 382.5
m/z
[Fe^II3(dpbt)2(CH3OH)]2+
cal. 388.00
Simulated
Observed
386.0 386.5 387.0 387.5 388.0 388.5 389.0
m/z
[Fe^II4O(Hdpbt)2]2+
cal. 407.95
Simulated
Observed
406.0 406.5 407.0 407.5 408.0 408.5 409.0 409.5
m/z
[Fe^II4O2(Hdpbt)2]2+
cal. 416.96
Simulated
Observed
415.0 415.5 416.0 416.5 417.0 417.5 418.0 418.5
m/z
[Fe^II4O(dpbt)2(CH3OH)]2+
cal. 423.96
Simulated
Observed
422.0 422.5 423.0 423.5 424.0 424.5 425.0
m/z
[Fe^III2Fe^II2O(dpbt)3]2+
cal. 552.00
Simulated
Observed
550.0 550.5 551.0 551.5 552.0 552.5 553.0 553.5 554.0
m/z
[Fe^III4O2(dpbt)3]2+
cal. 560.01
Simulated
Observed
558.5 559.0 559.5 560.0 560.5 561.0 561.5 562.0
m/z
[Fe^III3Fe^IIO(dpbt)3Cl]2+
cal. 569.48
Simulated
Observed
567.5 568.0 568.5 569.0 569.5 570.0 570.5 571.0 571.5 572.0
m/z
[Fe^III2Fe^II3O2(dpbt)3]2+
cal. 587.97
Simulated
Observed
586.0 586.5 587.0 587.5 588.0 588.5 589.0 589.5 590.0
m/z
[Fe^III3Fe^II2O2(dpbt)3Cl]2+
cal. 605.45
Simulated
Observed
604 605 606 607
m/z
[Fe^III4Fe^IIO2(dpbt)3Cl2]2+
cal. 622.93
Simulated
Observed
621 622 623 624 625 626
m/z
[Fe^III4Fe^IIO2(dpbt)4]2+
cal. 732.00
Simulated
Observed
730 731 732 733 734 735
m/z
[Fe^III4Fe^IIO2(dpbt)3(Hdpbt)Cl]2+
cal. 750.00
Simulated
Observed
748 749 750 751 752 753
m/z

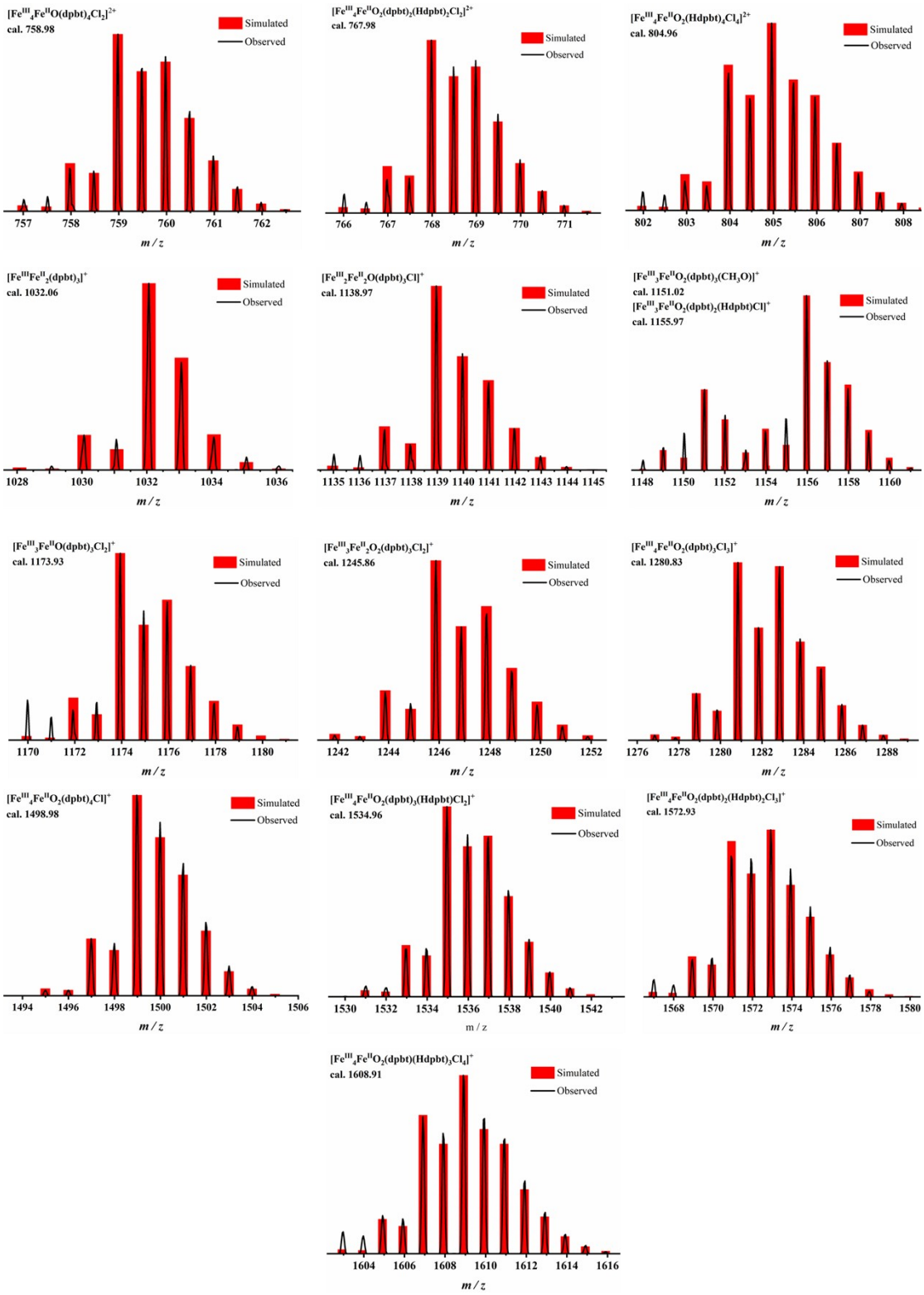
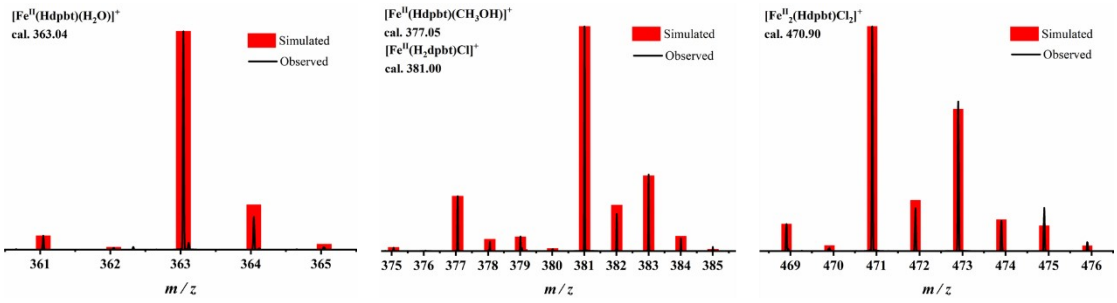


Fig. S10 The superposed simulated and observed spectra of time-dependent HRESI-MS species for **{Fe_5}-0D** in positive mode.

Table S4. Time-dependent HRESI-MS spectra assigned in the HRESI-MS of **{Fe_5}-0D** in positive mode.

m/z	Fragment	Relative Intensity						
		15 min	30 min	60 min	90 min	120 min	200 min	300 min
363.04	$[Fe^{II}(Hdpbt)H_2O]^+$ (*cal.* 363.04)	0.117	0.311	0.167	0.114	0.017	0.091	0
377.05	$[Fe^{II}(Hdpbt)(CH_3OH)]^+$ (*cal.*377.06)	0.244	0.138	0.105	0.023	0.015	0.018	0
381.00	$[Fe^{II}(H_2dpbt)Cl]^+$ (*cal.*381.06)	1	0.475	0.257	0.014	0.111	0.012	0
470.90	$[Fe^{II}_2(dpbt)Cl_2]^+$ (*cal.*470.90)	0.267	1	0.403	0.250	0.167	0.100	0
804.96	$[Fe^{III}_4Fe^{II}O_2(Hdpbt)_4Cl_4]^{2+}$ (*cal.*804.96)	0	0.140	0.229	0.391	0.606	1	1
1032.06	$[Fe^{III}Fe^{II}_2(dpbt)_3]^+$ (*cal.* 1032.06)	0	0.221	0.451	0.343	0.215	0.112	0
1138.97	$[Fe^{III}_4O(dpbt)_3Cl]^+$ (*cal.* 1138.97)	0	0.117	1	1	0.666	0.258	0
1155.96	$[Fe^{III}_3Fe^{II}O_2(dpbt)_3Cl+H]^+$ (*cal.* 1155.97)	0	0.066	0.179	0.091	0.139	0.052	0
1173.93	$[Fe^{III}_3Fe^{II}O(dpbt)_3Cl_2]^+$ (*cal.* 1173.93)	0	0.042	0.179	0.104	0.284	0.010	0
1245.85	$[Fe^{III}_3Fe^{II}_2O_2(dpbt)_3Cl_2]^+$ (*cal.* 1245.85)	0	0.075	0.262	0.480	0.164	0.052	0
1280.83	$[Fe^{III}_4Fe^{II}O_2(dpbt)_3Cl_3]^+$ (*cal.* 1280.83)	0	0.118	0.067	0.225	1	0.400	0
1608.91	$[Fe^{III}_4Fe^{II}O_2(dpbt)_4Cl_4+3H]^+$ (*cal.* 1608.91)	0	0	0	0.006	0	0.046	0.274



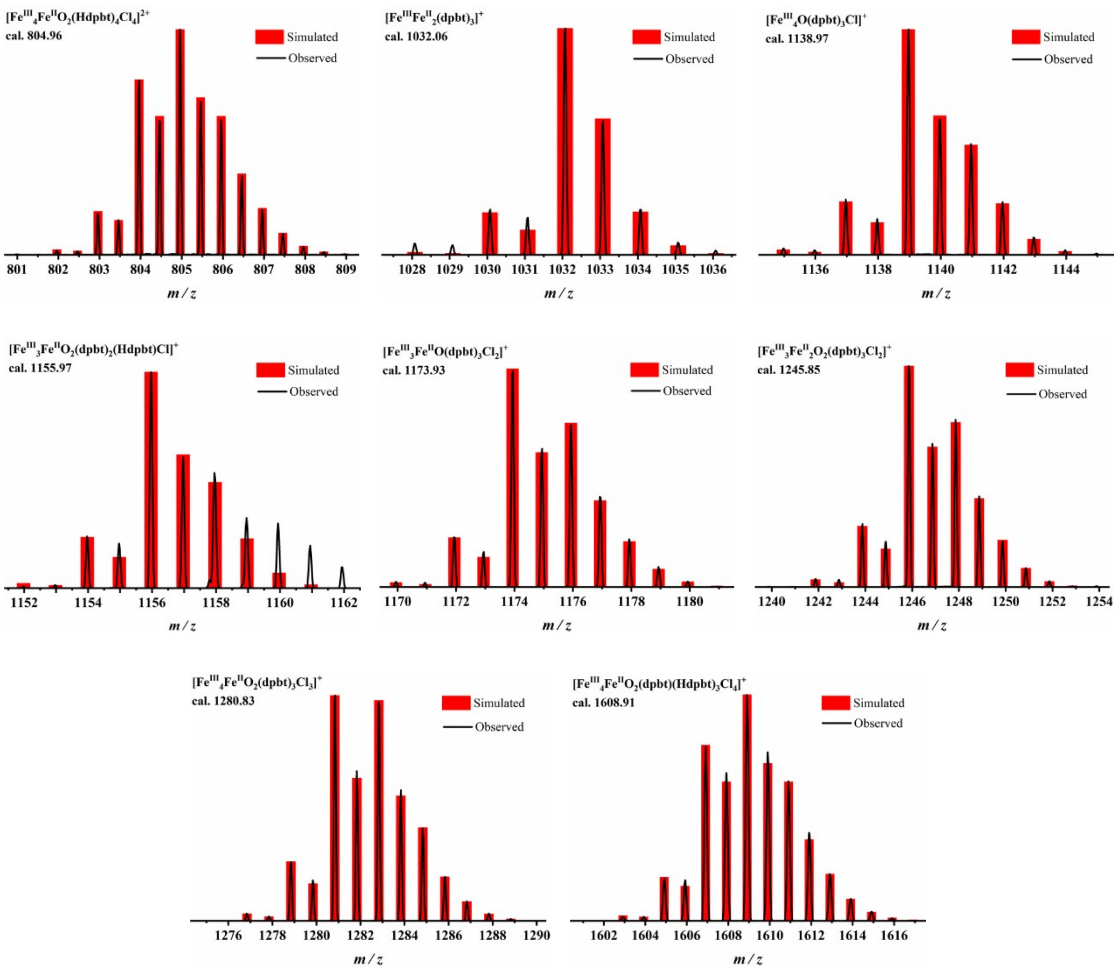
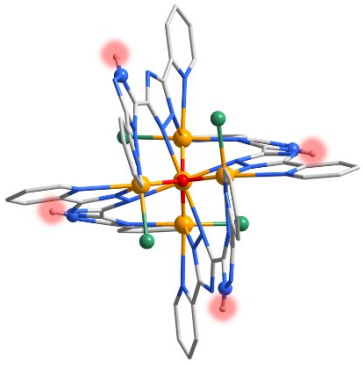


Fig. S11 The superposed simulated and observed spectra of time-dependent HRESI-MS species for **{Fe_5}-0D** in positive mode.



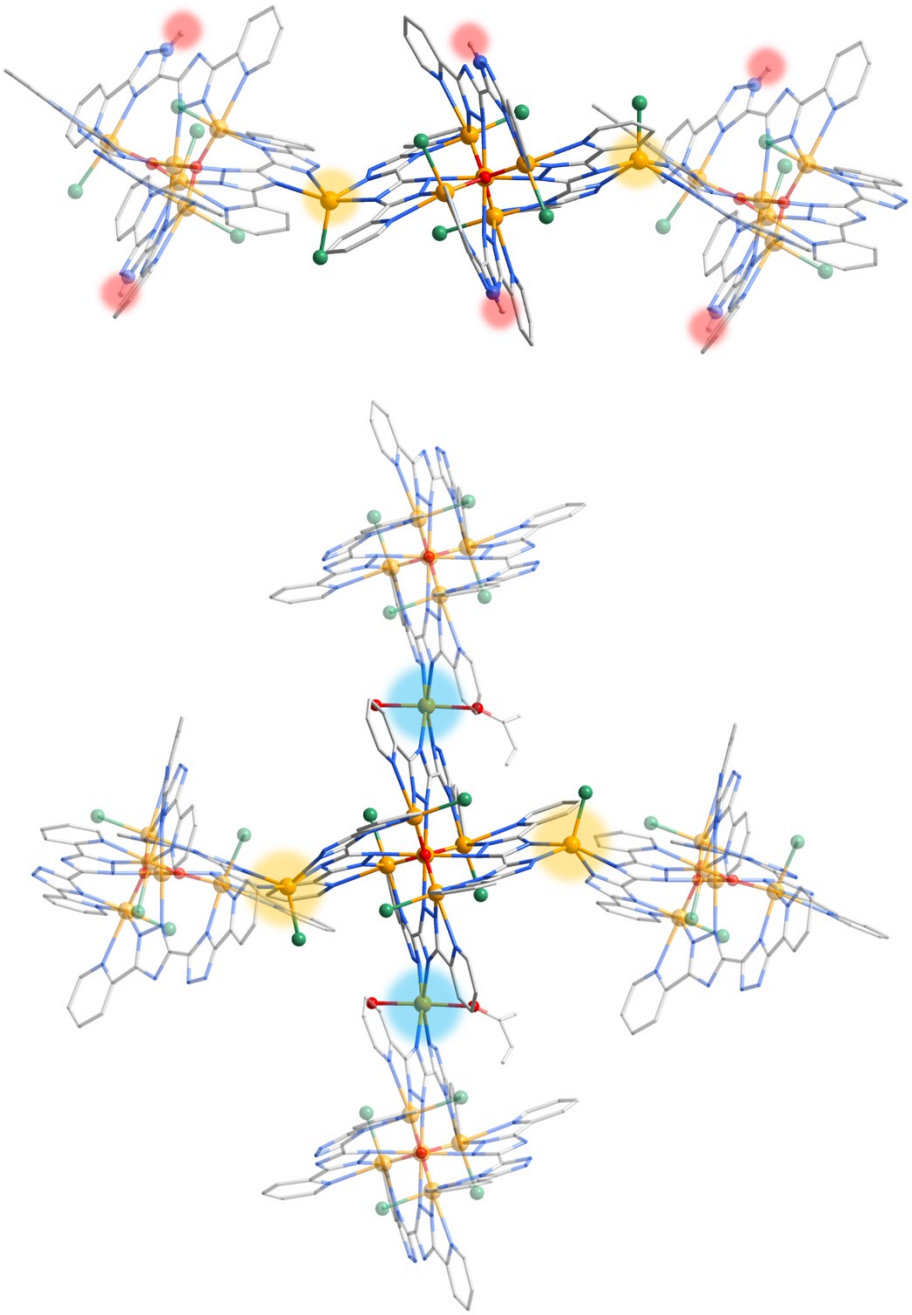


Fig. S12 Schematic diagram of dimension expansion from **{Fe_5}-0D** to **{Fe_5}-2D.** (All non-NH hydrogen atoms, methanol molecule and $FeCl_4^-$ anion are omitted for clarity.)

Table S5. Crystallographic data for **{Fe_5}-0D, {Fe_5}-1D, and {Fe_5}-2D (Squeeze)**

Identification code	**{Fe_5}-0D**	**{Fe_5}-1D**	**{Fe_5}-2D**
Empirical formula	$C_{56}H_{36}Cl_{12}Fe_7N_{32}O_6$	$C_{56}H_{34}Cl_9Fe_7N_{32}O_2$	$C_{58}H_{39}Cl_9Fe_8N_{32}O_4$
Formula weight (M)	2005.52	1897.15	2014.06
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	$P2_1/c$	$P2_1/n$
a (Å)	16.9840(11)	17.9866(12)	12.4532(2)
b (Å)	17.1651(11)	23.3546(12)	23.4463(5)

c (Å)	18.6317(11)	21.3135(13)	34.7967(6)
α (°)	77.606(5)	90	90
β (°)	67.810(6)	109.296(7)	95.1150(10)
γ (°)	77.930(5)	90	90
V/(Å^3)	4862.7(6)	8450.2(9)	10119.5(3)
Z	2	4	4
Dc(Mg m^{-3})	1.370	1.491	1.322
F(000)	1996	3780	4016
Reflections	39906/19855	60576/17260	71258/23678
collected/unique	R(int) = 0.0794	R(int) = 0.1204	R(int) = 0.0418
Goodness-of-fit on F^2	0.946	1.009	1.020
Final R indices $I > 2\sigma(I)$	$R_1 = 0.0778$ $\omega R_2 = 0.1776$	$R_1 = 0.0837$ $\omega R_2 = 0.1922$	$R_1 = 0.0624$ $\omega R_2 = 0.1438$
R indices	$R_1 = 0.1433$	$R_1 = 0.1849$	$R_1 = 0.0841$
(all data)	$\omega R_2 = 0.2173$	$\omega R_2 = 0.2548$	$\omega R_2 = 0.1544$

Table S6. Selected bond length and bond angle for **{Fe$_5$}-0D**, **{Fe$_5$}-1D**, and **{Fe$_5$}-2D**

{Fe$_5$}-0D.

Atomic Distances [Å]

Fe1—O1	2.213 (4)	Fe4—O2	1.830 (4)
Fe1—O2	2.189 (4)	Fe4—N21	2.156 (6)
Fe1—N4	2.170 (6)	Fe4—N24	2.221 (5)
Fe1—N14	2.208 (5)	Fe4—N31	2.045 (5)
Fe1—N20	2.160 (5)	Fe5—Cl3	2.306 (2)
Fe1—N30	2.203 (5)	Fe5—O2	1.855 (4)
Fe2—Cl2	2.3169 (18)	Fe5—N5	2.176 (6)
Fe2—O1	1.833 (4)	Fe5—N8	2.192 (5)
Fe2—N9	2.221 (5)	Fe5—N15	2.048 (5)
Fe2—N10	2.151 (5)	Fe5—N16	2.401 (5)
Fe2—N17	2.372 (5)	Fe6—Cl5	2.187 (2)
Fe2—N19	2.062 (6)	Fe6—Cl6	2.180 (3)
Fe3—Cl1	2.3126 (19)	Fe6—Cl7	2.178 (3)
Fe3—O1	1.862 (4)	Fe6—Cl8	2.184 (3)
Fe3—N1	2.393 (5)	Fe7—Cl9	2.189 (3)
Fe3—N3	2.061 (5)	Fe7—Cl10	2.180 (3)
Fe3—N25	2.232 (5)	Fe7—Cl11	2.161 (3)
Fe3—N26	2.157 (5)	Fe7—Cl12	2.171 (3)
Fe4—Cl4	2.301 (2)		

Bond Angles [°]

O2—Fe1—O1	179.52 (16)	N25—Fe3—N1	82.05 (19)
O2—Fe1—N14	90.23 (16)	N26—Fe3—Cl1	165.15 (15)
O2—Fe1—N30	88.64 (17)	N26—Fe3—N1	89.52 (18)
N4—Fe1—O1	90.34 (18)	N26—Fe3—N25	75.6 (2)
N4—Fe1—O2	90.13 (18)	O2—Fe4—Cl4	97.97 (14)
N4—Fe1—N14	89.46 (19)	O2—Fe4—N21	88.11 (19)
N4—Fe1—N30	90.58 (19)	O2—Fe4—N24	116.06 (18)
N14—Fe1—O1	89.89 (16)	O2—Fe4—N31	91.95 (18)
N20—Fe1—O1	88.58 (17)	N21—Fe4—Cl4	166.83 (16)
N20—Fe1—O2	90.95 (17)	N21—Fe4—N24	75.9 (2)
N20—Fe1—N4	178.9 (2)	N24—Fe4—Cl4	90.95 (16)
N20—Fe1—N14	90.94 (19)	N31—Fe4—Cl4	97.05 (15)
N20—Fe1—N30	89.05 (19)	N31—Fe4—N21	94.4 (2)
N30—Fe1—O1	91.24 (17)	N31—Fe4—N24	149.5 (2)
N30—Fe1—N14	178.9 (2)	Cl3—Fe5—N16	92.22 (14)
Cl2—Fe2—N17	88.33 (13)	O2—Fe5—Cl3	96.11 (14)
O1—Fe2—Cl2	98.49 (12)	O2—Fe5—N5	86.74 (18)
O1—Fe2—N9	113.87 (19)	O2—Fe5—N8	114.32 (18)
O1—Fe2—N10	88.45 (17)	O2—Fe5—N15	92.34 (18)
O1—Fe2—N17	161.94 (18)	O2—Fe5—N16	163.34 (18)
O1—Fe2—N19	90.67 (19)	N5—Fe5—Cl3	166.88 (15)
N9—Fe2—Cl2	89.96 (15)	N5—Fe5—N8	76.0 (2)
N9—Fe2—N17	82.7 (2)	N5—Fe5—N16	88.41 (18)
N10—Fe2—Cl2	164.87 (15)	N8—Fe5—Cl3	91.21 (18)
N10—Fe2—N9	74.93 (19)	N8—Fe5—N16	79.79 (18)
N10—Fe2—N17	89.07 (18)	N15—Fe5—Cl3	96.64 (16)
N19—Fe2—Cl2	92.61 (15)	N15—Fe5—N5	96.0 (2)
N19—Fe2—N9	154.7 (2)	N15—Fe5—N8	151.3 (2)
N19—Fe2—N10	100.77 (19)	N15—Fe5—N16	72.33 (18)
N19—Fe2—N17	72.23 (19)	Cl6—Fe6—Cl5	109.13 (11)
Cl1—Fe3—N1	89.25 (13)	Cl6—Fe6—Cl8	109.47 (12)
O1—Fe3—Cl1	97.50 (12)	Cl7—Fe6—Cl5	109.61 (10)
O1—Fe3—N1	162.93 (18)	Cl7—Fe6—Cl6	110.28 (12)
O1—Fe3—N3	91.92 (19)	Cl7—Fe6—Cl8	108.48 (14)

O1—Fe3—N25	113.53 (18)	Cl8—Fe6—Cl5	109.85 (13)
O1—Fe3—N26	87.85 (18)	Cl10—Fe7—Cl9	110.30 (13)
N3—Fe3—Cl1	93.84 (15)	Cl11—Fe7—Cl9	108.17 (12)
N3—Fe3—N1	71.9 (2)	Cl11—Fe7—Cl10	110.07 (13)
N3—Fe3—N25	153.7 (2)	Cl11—Fe7—Cl12	111.93 (14)
N3—Fe3—N26	99.83 (19)	Cl12—Fe7—Cl9	108.22 (12)
N25—Fe3—Cl1	89.53 (16)	Cl12—Fe7—Cl10	108.14 (13)

{Fe_5}-1D. Symmetry codes: (A) -*x*+1, *y*-1/2, -*z*+3/2.

Atomic Distances [Å]

Fe1—O1	2.253 (5)	Fe4—O2	1.828 (5)
Fe1—O2	2.218 (5)	Fe4—N21	2.101 (6)
Fe1—N4	2.147 (7)	Fe4—N24	2.224 (7)
Fe1—N14	2.182 (6)	Fe4—N31	2.061 (7)
Fe1—N20	2.125 (7)	Fe4—N32	2.406 (7)
Fe1—N30	2.208 (6)	Fe5—Cl3	2.303 (3)
Fe2—Cl2	2.295 (3)	Fe5—O2	1.850 (5)
Fe2—O1	1.837 (5)	Fe5—N5	2.128 (7)
Fe2—N9	2.255 (7)	Fe5—N8	2.202 (7)
Fe2—N10	2.176 (7)	Fe5—N15	2.048 (7)
Fe2—N17	2.412 (8)	Fe6—Cl5	2.245 (3)
Fe2—N19	2.049 (6)	Fe6—N2A	2.206 (7)
Fe3—Cl1	2.283 (3)	Fe6—N6A	2.076 (7)
Fe3—O1	1.836 (5)	Fe6—N18	2.324 (7)
Fe3—N1	2.367 (7)	Fe6—N22	2.055 (7)
Fe3—N3	2.057 (7)	Fe7—Cl6	2.168 (4)
Fe3—N25	2.245 (7)	Fe7—Cl7	2.186 (4)
Fe3—N26	2.152 (7)	Fe7—Cl8	2.198 (4)
Fe4—Cl4	2.311 (2)	Fe7—Cl9	2.152 (5)

Bond Angles [°]

O2—Fe1—O1	178.8 (2)	N26—Fe3—N1	85.6 (2)
N4—Fe1—O1	89.4 (2)	N26—Fe3—N25	74.5 (3)
N4—Fe1—O2	89.8 (2)	Cl4—Fe4—N32	87.08 (19)
N4—Fe1—N14	90.4 (2)	O2—Fe4—Cl4	99.98 (17)
N4—Fe1—N30	87.2 (2)	O2—Fe4—N21	88.3 (2)
N14—Fe1—O1	89.9 (2)	O2—Fe4—N24	113.2 (2)

N14—Fe1—O2	89.2 (2)	O2—Fe4—N31	92.6 (2)
N14—Fe1—N30	177.5 (2)	O2—Fe4—N32	164.2 (3)
N20—Fe1—O1	88.1 (2)	N21—Fe4—Cl4	165.6 (2)
N20—Fe1—O2	92.7 (2)	N21—Fe4—N24	75.9 (3)
N20—Fe1—N4	175.8 (2)	N21—Fe4—N32	88.0 (3)
N20—Fe1—N14	93.0 (2)	N24—Fe4—Cl4	89.9 (2)
N20—Fe1—N30	89.5 (2)	N24—Fe4—N32	80.7 (3)
N30—Fe1—O1	90.7 (2)	N31—Fe4—Cl4	96.53 (19)
N30—Fe1—O2	90.1 (2)	N31—Fe4—N21	94.9 (3)
Cl2—Fe2—N17	87.05 (18)	N31—Fe4—N24	152.0 (3)
O1—Fe2—Cl2	100.00 (17)	N31—Fe4—N32	72.5 (3)
O1—Fe2—N9	114.3 (2)	O2—Fe5—Cl3	100.54 (18)
O1—Fe2—N10	86.4 (2)	O2—Fe5—N5	87.9 (2)
O1—Fe2—N17	161.8 (3)	O2—Fe5—N8	115.7 (2)
O1—Fe2—N19	92.0 (2)	O2—Fe5—N15	91.5 (2)
N9—Fe2—Cl2	90.2 (2)	N5—Fe5—Cl3	165.6 (2)
N9—Fe2—N17	82.2 (3)	N5—Fe5—N8	74.6 (3)
N10—Fe2—Cl2	163.3 (2)	N8—Fe5—Cl3	91.2 (2)
N10—Fe2—N9	73.2 (3)	N15—Fe5—Cl3	94.3 (2)
N10—Fe2—N17	91.5 (2)	N15—Fe5—N5	97.3 (3)
N19—Fe2—Cl2	93.31 (19)	N15—Fe5—N8	150.8 (3)
N19—Fe2—N9	152.5 (3)	Cl5—Fe6—N18	95.74 (19)
N19—Fe2—N10	101.9 (3)	N2A—Fe6—Cl5	102.65 (19)
N19—Fe2—N17	70.7 (3)	N2A—Fe6—N18	157.5 (2)
Cl1—Fe3—N1	90.87 (18)	N6A—Fe6—Cl5	115.8 (2)
O1—Fe3—Cl1	100.37 (18)	N6A—Fe6—N2A	76.6 (3)
O1—Fe3—N1	161.3 (2)	N6A—Fe6—N18	107.0 (3)
O1—Fe3—N3	92.4 (3)	N22—Fe6—Cl5	122.9 (2)
O1—Fe3—N25	111.2 (3)	N22—Fe6—N2A	83.7 (3)
O1—Fe3—N26	87.1 (2)	N22—Fe6—N6A	120.8 (3)
N3—Fe3—Cl1	95.09 (19)	N22—Fe6—N18	75.4 (2)
N3—Fe3—N1	71.5 (3)	Cl6—Fe7—Cl7	110.08 (18)
N3—Fe3—N25	154.3 (3)	Cl6—Fe7—Cl8	108.40 (18)
N3—Fe3—N26	97.5 (3)	Cl7—Fe7—Cl8	109.91 (16)
N25—Fe3—Cl1	90.7 (2)	Cl9—Fe7—Cl6	108.5 (2)

N25—Fe3—N1	83.4 (3)	Cl9—Fe7—Cl7	108.1 (2)
N26—Fe3—Cl1	165.1 (2)	Cl9—Fe7—Cl8	111.8 (2)

{Fe_5}-2D. Symmetry codes: (A) -*x*+3/2, *y*-1/2, -*z*+3/2; (B) *x*-1, *y*, *z*.

Atomic Distances [Å]

Fe1—O1	2.178 (2)	Fe4—N32	2.432 (3)
Fe1—O2	2.171 (2)	Fe5—Cl3	2.2870 (11)
Fe1—N4	2.176 (3)	Fe5—O2	1.856 (2)
Fe1—N14	2.164 (3)	Fe5—N5	2.116 (3)
Fe1—N20	2.183 (3)	Fe5—N8	2.218 (3)
Fe1—N30	2.172 (3)	Fe5—N15	2.049 (3)
Fe2—Cl2	2.2969 (12)	Fe5—N16	2.436 (3)
Fe2—O1	1.849 (2)	Fe6—Cl5	2.2616 (17)
Fe2—N9	2.220 (3)	Fe6—N12A	2.094 (4)
Fe2—N10	2.109 (3)	Fe6—N13A	2.227 (3)
Fe2—N17	2.420 (3)	Fe6—N28	2.083 (3)
Fe2—N19	2.069 (3)	Fe6—N29	2.340 (3)
Fe3—Cl1	2.2963 (12)	Fe7—O3	2.120 (4)
Fe3—O1	1.853 (2)	Fe7—O4	2.140 (4)
Fe3—N3	2.058 (3)	Fe7—N2	2.272 (3)
Fe3—N25	2.242 (3)	Fe7—N6	2.155 (3)
Fe3—N26	2.096 (3)	Fe7—N18B	2.272 (3)
Fe4—Cl4	2.3090 (10)	Fe7—N22B	2.161 (3)
Fe4—O2	1.846 (2)	Fe8—Cl6	2.157 (3)
Fe4—N21	2.105 (3)	Fe8—Cl7	2.153 (3)
Fe4—N24	2.228 (3)	Fe8—Cl8	2.140 (3)
Fe4—N31	2.052 (3)	Fe8—Cl9	2.180 (4)

Bond Angles [°]

O1—Fe1—N20	89.56 (10)	N31—Fe4—Cl4	93.93 (9)
O2—Fe1—O1	179.61 (10)	N31—Fe4—N21	98.75 (12)
O2—Fe1—N4	90.80 (10)	N31—Fe4—N24	152.33 (12)
O2—Fe1—N20	90.58 (10)	N31—Fe4—N32	70.95 (11)
O2—Fe1—N30	89.93 (10)	Cl3—Fe5—N16	89.88 (9)
N4—Fe1—O1	89.06 (10)	O2—Fe5—Cl3	100.51 (8)
N4—Fe1—N20	178.57 (11)	O2—Fe5—N5	87.96 (11)
N14—Fe1—O1	90.84 (10)	O2—Fe5—N8	114.49 (11)

N14—Fe1—O2	89.52 (10)	O2—Fe5—N15	92.24 (11)
N14—Fe1—N4	89.88 (11)	O2—Fe5—N16	160.93 (11)
N14—Fe1—N20	90.51 (11)	N5—Fe5—Cl3	165.87 (9)
N14—Fe1—N30	179.44 (11)	N5—Fe5—N8	75.43 (11)
N30—Fe1—O1	89.70 (10)	N5—Fe5—N16	85.33 (12)
N30—Fe1—N4	89.98 (11)	N8—Fe5—Cl3	90.70 (9)
N30—Fe1—N20	89.63 (11)	N8—Fe5—N16	81.00 (11)
Cl2—Fe2—N17	87.85 (10)	N15—Fe5—Cl3	95.90 (9)
O1—Fe2—Cl2	99.68 (9)	N15—Fe5—N5	95.04 (12)
O1—Fe2—N9	114.70 (12)	N15—Fe5—N8	150.82 (12)
O1—Fe2—N10	88.41 (11)	N15—Fe5—N16	70.65 (12)
O1—Fe2—N17	161.93 (12)	Cl5—Fe6—N29	98.88 (10)
O1—Fe2—N19	92.07 (11)	N12A—Fe6—Cl5	117.86 (12)
N9—Fe2—Cl2	90.77 (10)	N12A—Fe6—N13A	77.11 (12)
N9—Fe2—N17	81.34 (12)	N12A—Fe6—N29	101.05 (12)
N10—Fe2—Cl2	165.58 (9)	N13A—Fe6—Cl5	101.73 (10)
N10—Fe2—N9	74.96 (13)	N13A—Fe6—N29	157.50 (12)
N10—Fe2—N17	87.95 (12)	N28—Fe6—Cl5	119.47 (12)
N19—Fe2—Cl2	93.15 (9)	N28—Fe6—N12A	122.42 (14)
N19—Fe2—N9	151.87 (13)	N28—Fe6—N13A	86.79 (12)
N19—Fe2—N10	98.50 (12)	N28—Fe6—N29	75.21 (12)
N19—Fe2—N17	71.00 (11)	O3—Fe7—O4	172.71 (17)
O1—Fe3—Cl1	99.13 (9)	O3—Fe7—N2	84.02 (13)
O1—Fe3—N3	92.10 (11)	O3—Fe7—N6	98.33 (15)
O1—Fe3—N25	115.51 (12)	O3—Fe7—N18B	95.24 (14)
O1—Fe3—N26	87.68 (12)	O3—Fe7—N22B	85.56 (16)
N3—Fe3—Cl1	94.04 (10)	O4—Fe7—N2	90.28 (15)
N3—Fe3—N25	150.88 (13)	O4—Fe7—N6	84.62 (14)
N3—Fe3—N26	98.55 (12)	O4—Fe7—N18B	82.05 (13)
N25—Fe3—Cl1	90.64 (10)	O4—Fe7—N22B	100.22 (17)
N26—Fe3—Cl1	165.47 (9)	N6—Fe7—N2	75.81 (11)
N26—Fe3—N25	74.82 (13)	N6—Fe7—N18B	166.38 (14)
Cl4—Fe4—N32	89.54 (8)	N6—Fe7—N22B	104.31 (12)
O2—Fe4—Cl4	99.68 (8)	N18B—Fe7—N2	106.93 (11)
O2—Fe4—N21	88.34 (11)	N22B—Fe7—N2	169.48 (15)

O2—Fe4—N24	114.06 (11)	N22B—Fe7—N18B	75.50 (11)
O2—Fe4—N31	92.41 (11)	Cl6—Fe8—Cl9	110.28 (12)
O2—Fe4—N32	161.60 (11)	Cl7—Fe8—Cl6	107.83 (15)
N21—Fe4—Cl4	164.71 (9)	Cl7—Fe8—Cl9	110.36 (19)
N21—Fe4—N24	75.26 (12)	Cl8—Fe8—Cl6	111.68 (17)
N21—Fe4—N32	86.58 (12)	Cl8—Fe8—Cl7	109.09 (18)
N24—Fe4—Cl4	89.55 (9)	Cl8—Fe8—Cl9	107.62 (15)
N24—Fe4—N32	81.66 (11)		

Mask results for {Fe_5}-0D, {Fe_5}-1D, and {Fe_5}-2D are as follows:

$[Fe^{III}_4Fe^{II}O_2Cl_4(Hdpbt)_4]\cdot[Fe^{III}Cl_4]_2\cdot$4.5MeOH ({$Fe_5$}-0D)

loop_

_smtbx_masks_void_nr

_smtbx_masks_void_average_x

_smtbx_masks_void_average_y

_smtbx_masks_void_average_z

_smtbx_masks_void_volume

_smtbx_masks_void_count_electrons

_smtbx_masks_void_content

1 0.000 0.000 0.000 1477.5 165.9

That is, SQUEEZE gives 165.9 electrons/unit cell for the voids. If these electrons are all from MeOH (18e^-), each unit cell has 165.9/18 ≈ 9 MeOH molecules, and each formula unit has 4.5 MeOH molecules (since Z = 2). So the suitable formula for this compound should be $[Fe^{III}_4Fe^{II}O_2Cl_4(Hdpbt)_4]\cdot[Fe^{III}Cl_4]_2\cdot$4.5MeOH

$\{[Fe^{III}_4Fe^{II}_2O_2Cl_5(dpbt)_2(Hdpbt)_2]\cdot(Fe^{III}Cl_4)\cdot$6MeOH$\}_n$ ({Fe_5}-1D)

loop_

_smtbx_masks_void_nr

_smtbx_masks_void_average_x

_smtbx_masks_void_average_y

_smtbx_masks_void_average_z

_smtbx_masks_void_volume

_smtbx_masks_void_count_electrons

_smtbx_masks_void_content

1 -0.118 0.250 0.049 1113.8 212.3 ?

2 -0.857 0.750 0.162 1113.8 209.4 ?

That is, SQUEEZE gives 421.7 electrons/unit cell for the voids. If these electrons are all from MeOH (18e^-), each unit cell has 421.7/18 ≈ 23.4 MeOH molecules, and each formula unit has 6 MeOH molecules (since Z = 4). So the suitable formula for this compound should be $\{[Fe^{III}_4Fe^{II}_2O_2Cl_5(dpbt)_2(Hdpbt)_2]\cdot(Fe^{III}Cl_4)\cdot$6MeOH$\}_n$

$\{[Fe^{III}_4Fe^{II}_3O_2Cl_5(dpbt)_4(H_2O)_{1.5}(MEK)_{0.5}]\cdot(Fe^{III}Cl_4)\cdot$8.5MeOH$\}_n$ ({Fe_5}-2D)

loop_

_smtbx_masks_void_nr

_smtbx_masks_void_average_x

_smtbx_masks_void_average_y

_smtbx_masks_void_average_z

_smtbx_masks_void_volume

_smtbx_masks_void_count_electrons

_smtbx_masks_void_content

1 -0.099 -0.404 0.401 3478.1 608.4 ?

That is, SQUEEZE gives 608.4 electrons/unit cell for the voids. If these electrons are all from MeOH (18e^-), each unit cell has 608.4/18 = 33.8 MeOH molecules, and each formula unit has 8.5 MeOH molecules (since Z = 4). So the suitable formula for this compound should be $\{[Fe^{III}_4Fe^{II}_3O_2Cl_5(dpbt)_4(H_2O)_{1.5}(MEK)_{0.5}]\cdot(Fe^{III}Cl_4)\cdot$8.5MeOH$\}_n$