

## Supporting Information

### Pentanuclear Clusters Resembling the Cubane-Dangler Connectivity in Native Oxygen-Evolving Center of Photosystem II

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#### Experimental section

##### Materials and methods

All chemicals were obtained commercially without further purification. *Caution! Although no such sign was observed during the present work, perchlorate salts are potentially explosive and should be handled with care and in small quantities.*

Elemental analysis (C, H and N) was carried out using a Perkin-Elmer 2400 Elemental Analyzer. ICP-AES analyses were performed on a PerkinElmer OPTIMA 3300DV ICP spectrometer. Electrospray mass spectrometry (ESI-MS) measurements were carried out in the positive ion mode using an Orbitrap Fusion™ Tribrid™ mass spectrometer (Thermo Scientific, San Jose, CA, USA) that was equipped with an electrospray ionization (ESI) source. Mass spectra were collected in the mass range  $m/z$  200-2000. The heated ion capillary was maintained at 320 °C. The electrochemical measurements were conducted on a Bio-Logic VSP electrochemical workstation. Cyclic voltammograms were recorded on ca. 1 mM solutions of the relevant complexes at 25 °C with a platinum wire counter electrode, a Ag/Ag<sup>+</sup> reference electrode (0.01 M AgNO<sub>3</sub>, 0.1 M nBu<sub>4</sub>NPF<sub>6</sub> in CH<sub>3</sub>CN), and a 3.0 mm glassy carbon electrode disc. The electrolyte solutions were 0.1 M nBu<sub>4</sub>NPF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub>:DMF (20:1) for all compounds. All reported values are referenced to an internal ferrocene/ferrocenium couple.

Single-crystal X-ray diffraction measurements for compound 1 and 3 were carried out using a Bruker D8 QUEST system with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 150 K. Data of compound 4 were collected on a MarCCD mx300 in the National Center for Protein Sciences Shanghai at the Shanghai Synchrotron Radiation Facility at 100 K. The diffraction data of compound 4 were transformed by APEX3 (The file type of the diffraction pictures was changed from name.mccd to name.sfrm). The raw data collection and reduction were done using APEX3 software.<sup>1</sup> Absorption corrections were applied using SADABS. The structures were solved by direct methods and refined by full-matrix least-squares techniques based on F2 using the SHELXS-2014 program.<sup>2</sup> All the non-hydrogen atoms were refined with anisotropic parameters. Program SQUEEZE, a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data.<sup>3</sup>

## Synthesis

2-(hydroxy(bipyridin-2-yl)methyl)phenol (H<sub>2</sub>L) was synthesized according to the literature.<sup>4</sup>

### Preparation of [Fe<sup>III</sup><sub>3</sub>Zn<sup>II</sup><sub>2</sub>L<sub>3</sub>O(OAc)<sub>3</sub>(CH<sub>3</sub>OH)](ClO<sub>4</sub>)<sub>2</sub>·(CH<sub>3</sub>OH)<sub>1.5</sub> (compound 1)

A solution of Fe(ClO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O (105mg, 0.3mmol) in CH<sub>3</sub>OH (5mL) was added with stirring to a solution of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (74mg, 0.3mmol) and H<sub>2</sub>L (28mg, 0.2mmol) in CH<sub>3</sub>OH (10mL), followed by addition of Et<sub>3</sub>N (15 μL). After stirring for 2 h, the resulting dark-red solution was filtered and the filtrate was left undisturbed to slowly evaporate. After 4 days, black orthohexagonal crystals were obtained in ca. 22% yield (based on Fe). Elemental analysis (%) Calcd for [Fe<sup>III</sup><sub>3</sub>Mn<sup>II</sup><sub>2</sub>L<sub>3</sub>O(OAc)<sub>3</sub>(CH<sub>3</sub>OH)(ClO<sub>4</sub>)<sub>2</sub>]·(CH<sub>3</sub>OH)<sub>1.5</sub> (C<sub>59.5</sub>H<sub>55</sub>N<sub>6</sub>O<sub>23.5</sub>Cl<sub>2</sub>Fe<sub>3</sub>Zn<sub>2</sub>) : C 44.68, H 3.44, N 5.23, Fe 10.51, Zn 8.14; found: C 45.96, H 3.57, N 5.19, Fe 10.22, Zn 8.09.

### Preparation of compound 2

A solution of Fe(ClO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O (70mg, 0.2mmol) in CH<sub>3</sub>OH (5mL) was added with stirring to a solution of Co(OAc)<sub>2</sub> (74mg, 0.3mmol) and H<sub>2</sub>L (28mg, 0.2mmol) in CH<sub>3</sub>OH (5mL), followed by addition of Et<sub>3</sub>N (15 μL). After stirring for 2 h, the resulting dark-red solution was filtered and the filtrate was left undisturbed to slowly evaporate. After 4 days, black orthohexagonal crystals were obtained in ca. 13% yield (based on Fe). Elemental analysis (%) found for compound 2: C 45.32, H 3.88, N 5.03, Fe 10.32, Co 7.39.

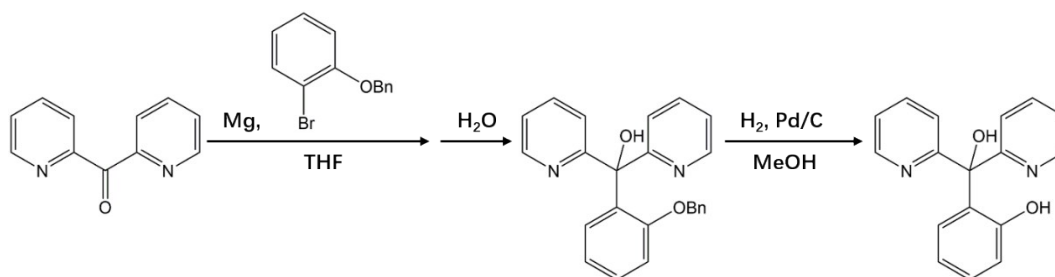
### Preparation of [Fe<sup>III</sup><sub>3</sub>Mn<sup>II</sup><sub>2</sub>L<sub>3</sub>O(OAc)<sub>3</sub>(CH<sub>3</sub>OH)](ClO<sub>4</sub>)<sub>2</sub>·(CH<sub>3</sub>OH)<sub>1.5</sub> (compound 3)

A solution of Fe(ClO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O (70mg, 0.2mmol) in CH<sub>3</sub>OH (5mL) was added with stirring to a solution of Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O (74mg, 0.3mmol) and H<sub>2</sub>L (28mg, 0.1mmol) in CH<sub>3</sub>OH (5mL), followed by addition of Et<sub>3</sub>N (20 μL). After stirring for 2 h, the resulting dark-red solution was filtered and the filtrate was left undisturbed to slowly evaporate. After 4 days, black orthohexagonal crystals were obtained in ca. 27% yield (based on Fe). Elemental analysis (%) Calcd for [Fe<sup>III</sup><sub>3</sub>Mn<sup>II</sup><sub>2</sub>L<sub>3</sub>O(OAc)<sub>3</sub>(CH<sub>3</sub>OH)(ClO<sub>4</sub>)<sub>2</sub>]·(CH<sub>3</sub>OH)<sub>1.5</sub> (C<sub>59.5</sub>H<sub>55</sub>N<sub>6</sub>O<sub>23.5</sub>Cl<sub>2</sub>Fe<sub>3</sub>Mn<sub>2</sub>) : C 45.25, H 3.49, N 5.32, Fe 10.65, Mn 6.97; found: C 46.03, H 3.65, N 5.22, Fe 10.43, Mn 6.82.

### Preparation of [Fe<sup>III</sup><sub>3</sub>Ni<sup>II</sup><sub>2</sub>L<sub>3</sub>O(OAc)<sub>2</sub>(OCH<sub>3</sub>)(CH<sub>3</sub>OH)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub> (compound 4)

A solution of Fe(ClO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O (70mg, 0.2mmol) in CH<sub>3</sub>OH (5mL) was added with stirring to a solution of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (74mg, 0.3mmol) and H<sub>2</sub>L (28mg, 0.2mmol) in CH<sub>3</sub>OH (5mL), followed by addition of Et<sub>3</sub>N (15 μL). After stirring for 2 h, the resulting deep red solution was filtered and the filtrate was left undisturbed to slowly evaporate. After a week, dark red block crystals were obtained in ca. 9% yield (based on Fe). Elemental analysis (%) Calcd for Fe<sup>III</sup><sub>3</sub>Ni<sup>II</sup><sub>2</sub>L<sub>3</sub>O(OAc)<sub>2</sub>(OCH<sub>3</sub>)(CH<sub>3</sub>OH)(H<sub>2</sub>O)(ClO<sub>4</sub>)<sub>2</sub> (C<sub>57</sub>H<sub>48</sub>Cl<sub>2</sub>Fe<sub>3</sub>N<sub>6</sub>Ni<sub>2</sub>O<sub>22</sub>) : C 44.85, H 3.15, N 5.51, Fe 11.02, Ni 7.74; found: C 46.18, H 3.83, N 5.01, Fe 10.53, Ni 7.55.

Scheme S1. Synthetic route of H<sub>2</sub>L.

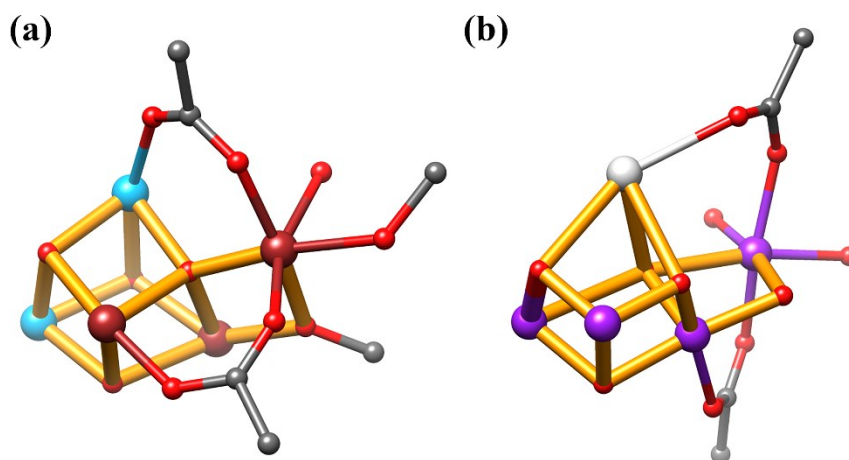


**Table S1** Crystallographic data for **1**, **3** and **4**

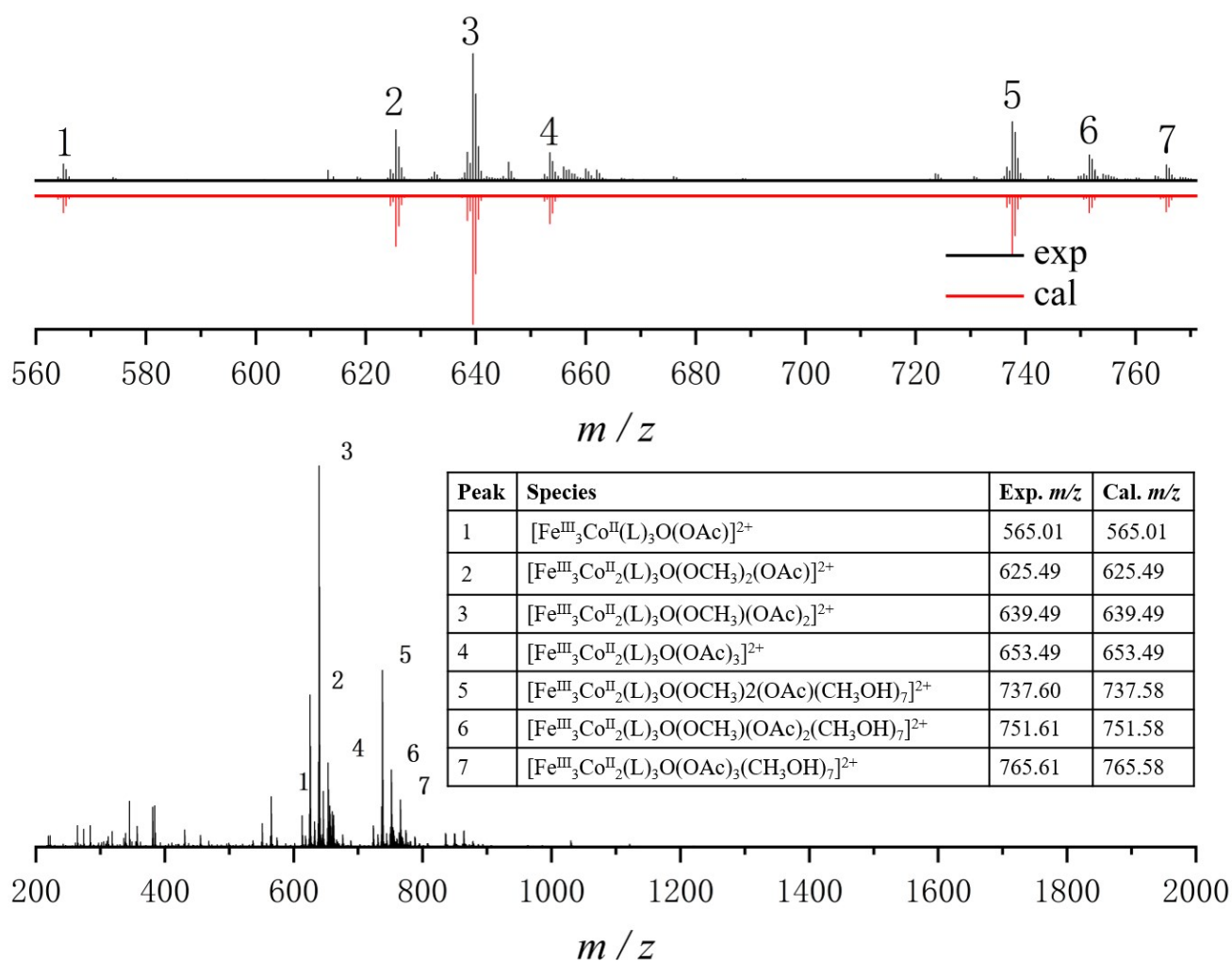
compound	1	3	4
Empirical formula	C <sub>119</sub> H <sub>110</sub> Cl <sub>4</sub> Fe <sub>6</sub> N <sub>12</sub> O <sub>47</sub> Zn <sub>4</sub>	C <sub>119</sub> H <sub>110</sub> Cl <sub>4</sub> Fe <sub>6</sub> Mn <sub>4</sub> N <sub>12</sub> O <sub>47</sub>	C <sub>57</sub> H <sub>48</sub> Cl <sub>2</sub> Fe <sub>3</sub> N <sub>6</sub> Ni <sub>2</sub> O <sub>22</sub>
Formula weight	3198.56	3156.84	1524.88
Temperature/K	150.(2)	150.(2)	273(2)
Crystal system	trigonal	trigonal	triclinic
Space group	R $\bar{3}$	R $\bar{3}$	p $\bar{1}$
a/Å	13.0721(3)	13.1328(3)	14.1061(10)
b/Å	13.0721(3)	13.1328(3)	14.4531(9)
c/Å	63.6995(19)	63.2624(19)	17.9914(12)
$\alpha$ /°	90	90	79.977(2)
$\beta$ /°	90	90	68.320(2)
$\gamma$ /°	120	120	72.495(2)
Volume/Å <sup>3</sup>	9426.6(5)	9449.1(5)	3242.5(4)
Z	3	3	2
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.690	1.664	1.562
$\mu/\text{mm}^{-1}$	1.601	1.236	1.387
F(000)	4884.0	4824.0	1552.0
Crystal size/mm <sup>3</sup>	0.140 × 0.130 × 0.130	0.140 × 0.120 × 0.110	0.140 × 0.120 × 0.110
Radiation	MoK $\alpha$ ( $\lambda$ = 0.71073)	MoK $\alpha$ ( $\lambda$ = 0.71073)	MoK $\alpha$ ( $\lambda$ = 0.71073)
2 $\theta$ range for data collection/°	4.82 to 50.08	4.82 to 50.16	2.442 to 56.546
Index ranges	-12 ≤ h ≤ 11, -15 ≤ k ≤ 15, -42 ≤ l ≤ 75	-10 ≤ h ≤ 9, -15 ≤ k ≤ 15, -75 ≤ l ≤ 37	-17 ≤ h ≤ 17, -19 ≤ k ≤ 19, -23 ≤ l ≤ 23
Reflections collected	10641	10528	45714
Independent reflections	3702 [R <sub>int</sub> = 0.0315, R <sub>sigma</sub> = 0.0393]	3721 [R <sub>int</sub> = 0.0270, R <sub>sigma</sub> = 0.0344]	12537 [R <sub>int</sub> = 0.0827, R <sub>sigma</sub> = 0.0498]
Data/restraints/parameters	3702/13/317	3721/14/311	12537/276/804
Goodness-of-fit on F <sup>2</sup>	1.031	1.081	1.039
Final R indexes [I ≥ 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0406, wR <sub>2</sub> = 0.0957	R <sub>1</sub> = 0.0526, wR <sub>2</sub> = 0.1300	R <sub>1</sub> = 0.0969, wR <sub>2</sub> = 0.2467
Final R indexes [all data]	R <sub>1</sub> = 0.0530, wR <sub>2</sub> = 0.1016	R <sub>1</sub> = 0.0689, wR <sub>2</sub> = 0.1388	R <sub>1</sub> = 0.1184, wR <sub>2</sub> = 0.2709
Largest diff. peak/hole / e Å <sup>-3</sup>	1.00/-1.45	1.80/-0.77	1.87/-2.85

**Table S2** Fe-O/Fe-N and Ni-O/Ni-N bond distance (Å) and calculated Fe/Ni valences<sup>5</sup> for compound **4**

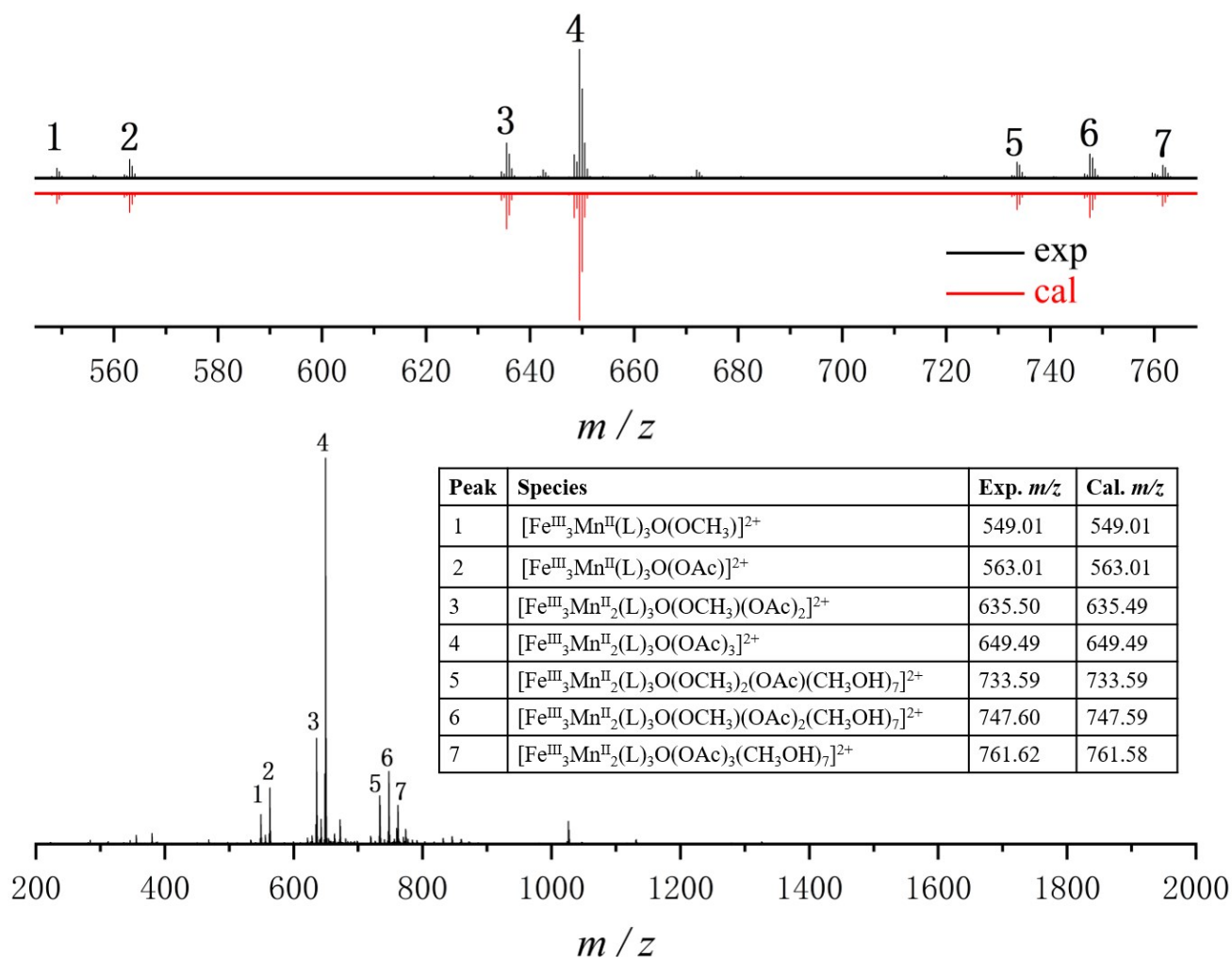
Bond	Length/Å	Bond	Length/Å	Bond	Length/Å	Bond	Length/Å	Bond	Length/Å
Fe1-O2	1.851(5)	Fe2-O4	1.894(5)	Fe3-O12	1.895(5)	Ni1-O5	2.026(4)	Ni2-O1	2.021(5)
Fe1-O7	1.988(5)	Fe2-O6	1.965(6)	Fe3-O10	1.982(7)	Ni1-N3	2.059(5)	Ni2-O9	2.030(5)
Fe1-O12	2.012(5)	Fe2-O11	1.993(6)	Fe3-O11	1.986(6)	Ni1-N5	2.085(6)	Ni2-N6	2.051(6)
Fe1-O3	2.048(5)	Fe2-O12	2.054(5)	Fe3-O8	1.996(6)	Ni1-N1	2.090(6)	Ni2-O12	2.085(4)
Fe1-O1	2.080(4)	Fe2-O5	2.116(5)	Fe3-O13	2.076(7)	Ni1-O1	2.112(4)	Ni2-N2	2.114(5)
Fe1-N4	2.187(6)	Fe2-O3	2.232(5)	Fe3-O14	2.106(6)	Ni1-O3	2.126(5)	Ni2-O5	2.147(4)
Average	2.028	Average	2.032	Average	2.007	Average	2.083	Average	2.075
<b>Calculated Fe/Ni valences</b>									
Fe1	+3(0.074)	Fe2	+3(0.090)	Fe3	+3(0.124)	Ni1	+2(0.070)	Ni2	+2(0.100)



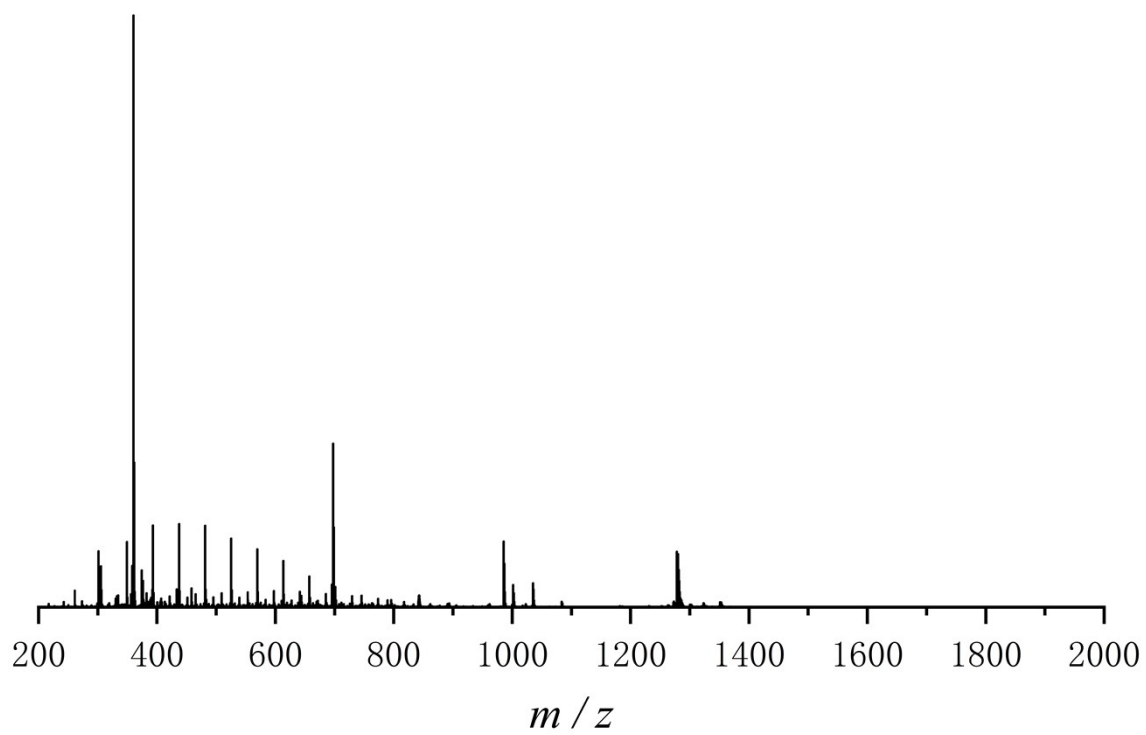
**Figure S1.** “Cubane-plus-dangler” structures of compound **4** (a) and the native OEC (b), highlighting the coordination environment of the dangling ions and their connectivity with the parent cubane core. (Fe: dark red; Ni: light blue; Ca: light gray; Mn: purple; C: dim gray; O: red)



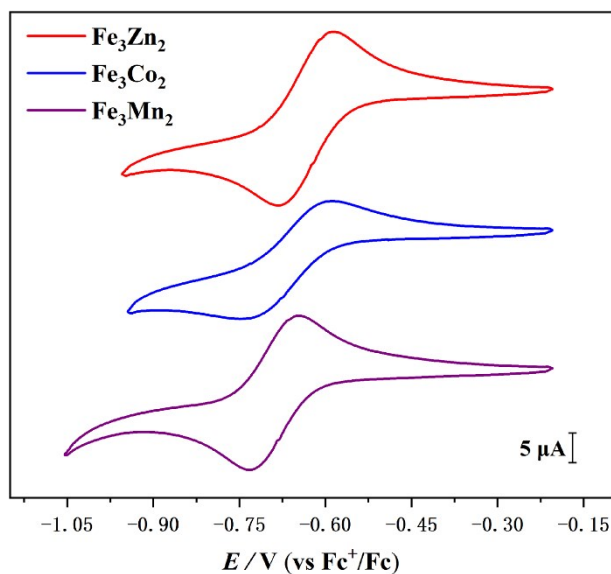
**Figure S2.** ESI-MS of compound **2** in DCM/DMF (20:1). Charge states are indicated as  $2^+$ . Experimental (black) and simulated (red) mass spectra of the isotopic envelopes are exhibited. The formulas of each species are given in the table.



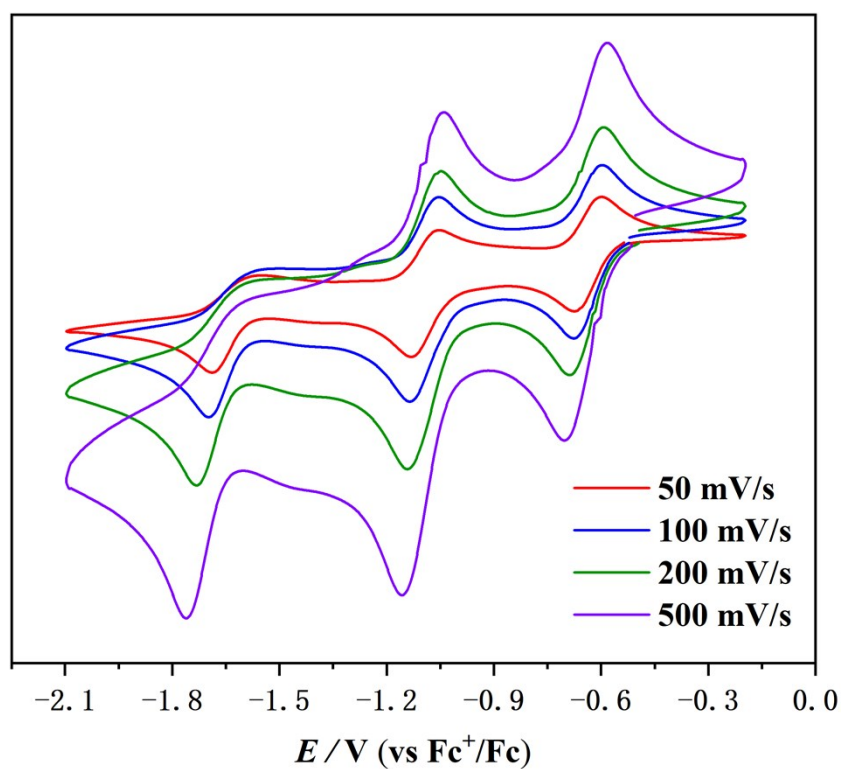
**Figure S3.** ESI-MS of compound **3** in DCM/DMF (20:1). Charge states are indicated as  $2^+$ . Experimental (black) and simulated (red) mass spectra of the isotopic envelopes are exhibited. The formulas of each species are given in the table.



**Figure S4.** ESI-MS of compound **4** dissolved in DCM/DMF (20:1).

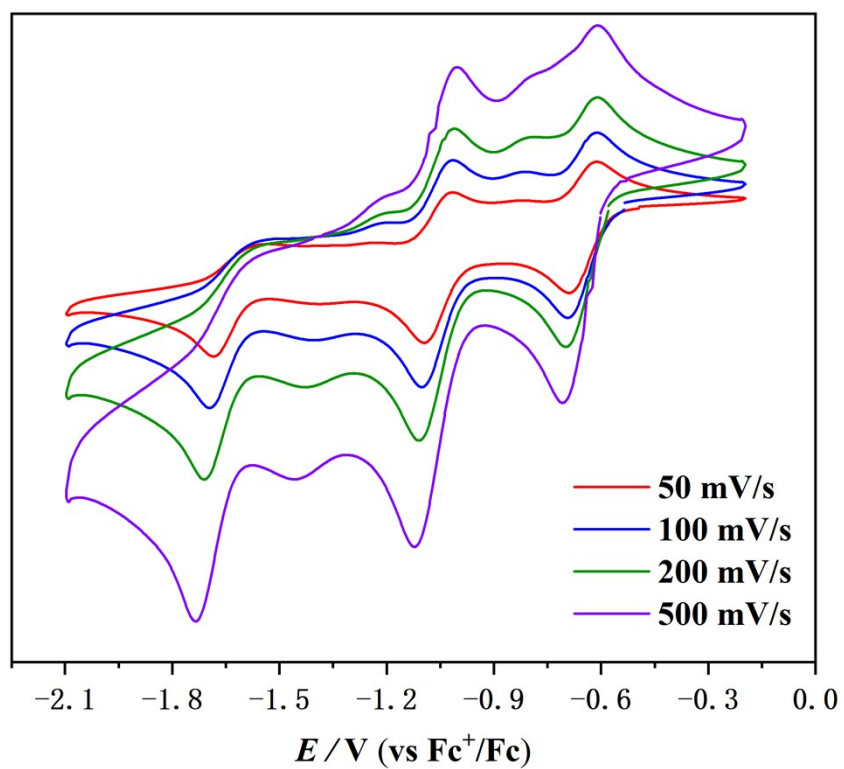


**Fig. S5** Cyclic voltammograms corresponding to the  $[\text{Fe}^{\text{III}}_3\text{M}^{\text{II}}_2]/[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{M}^{\text{II}}_2]$  redox couple ( $\text{M}^{\text{II}} = \text{Zn}^{\text{II}}, \text{Co}^{\text{II}}, \text{and Mn}^{\text{II}}$ ) in DCM/DMF (20:1). Scan rate is 100 mV/s. Potentials are referenced to  $\text{Fc}^+/\text{Fc}$ .

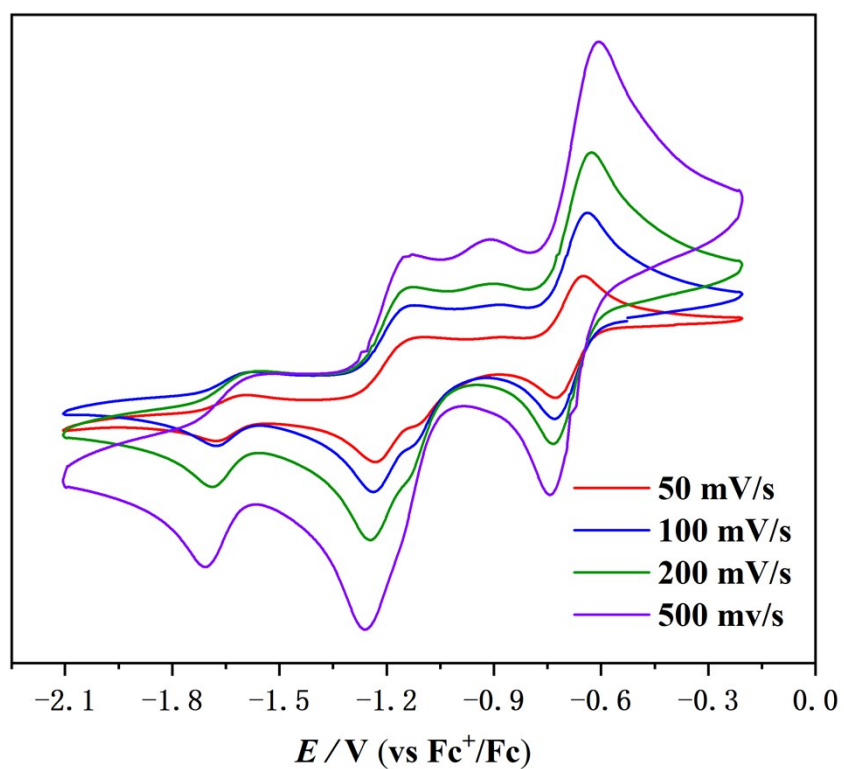


**Figure S6.** Cyclic voltammograms with varying scan rates of compound **1** ( $\text{Fe}_3\text{Zn}_2$ ).

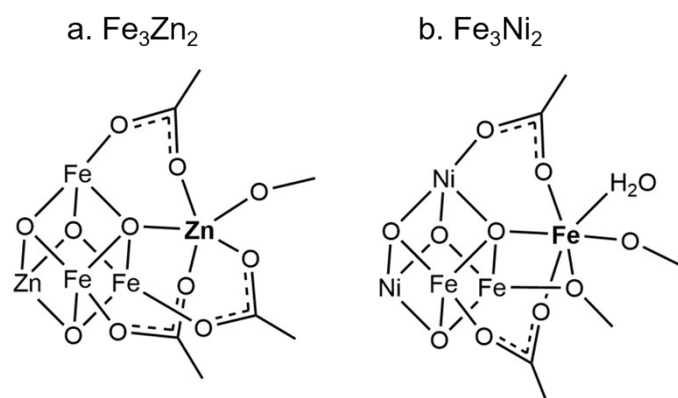




**Figure S7.** Cyclic voltammograms with varying scan rates of compound 2 ( $\text{Fe}_3\text{Co}_2$ ).



**Figure S8.** Cyclic voltammograms with varying scan rates of compound 3 ( $\text{Fe}_3\text{Mn}_2$ ).



**Figure S9.** ChemDraws for compound **1** (a) and compound **4** (b). (Ligands are omitted for clarity.)

## References

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