Supporting Information for

Optimize the Proton Conductivity of Fe–Diphosphonates by Increasing the Relative Number of Protons and Carrier Densities

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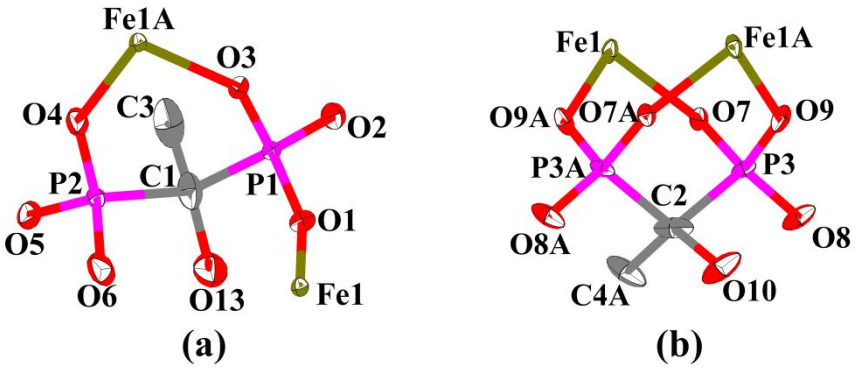

Figure S1. The coordination mode of HEDP for compound **1** (Hydrogen atoms are omitted for clarity).

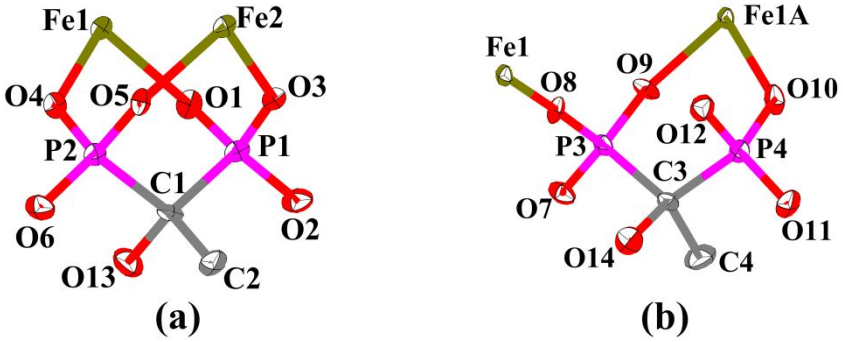

Figure S2. The coordination mode of HEDP for compound **2** (Hydrogen atoms are omitted for clarity).

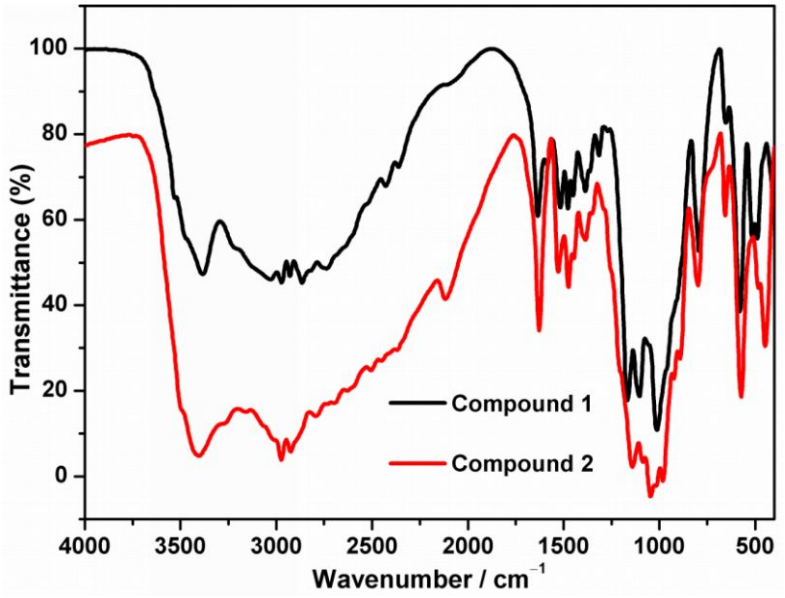

Figure S3. IR plot of **1** and **2**.

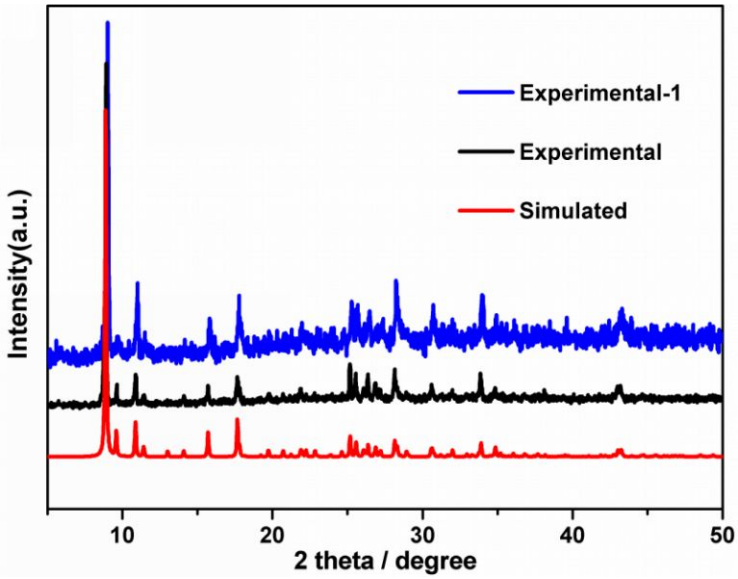

Figure S4. The PXRD plot of compound **1**, the data named *Experimental-1* is the sample after proton-conducting measurement.

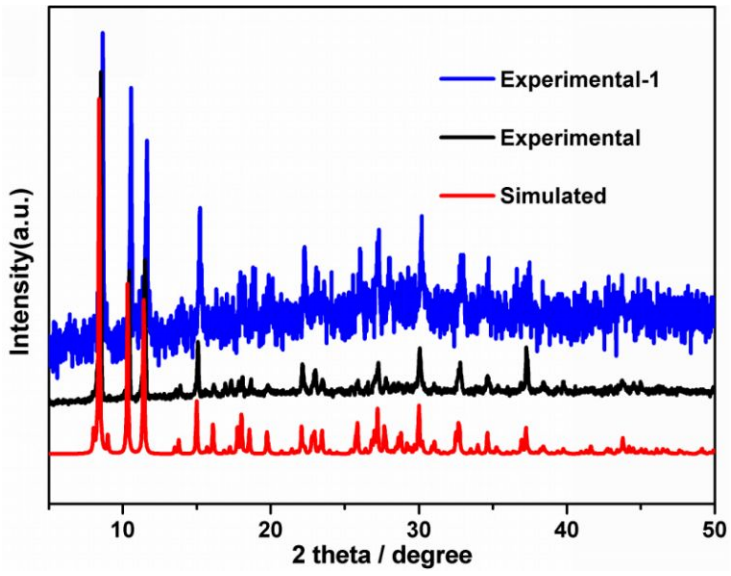

Figure S5. The PXRD plot of compound **2**, the data named *Experimental-1* is the sample after proton-conducting measurement.

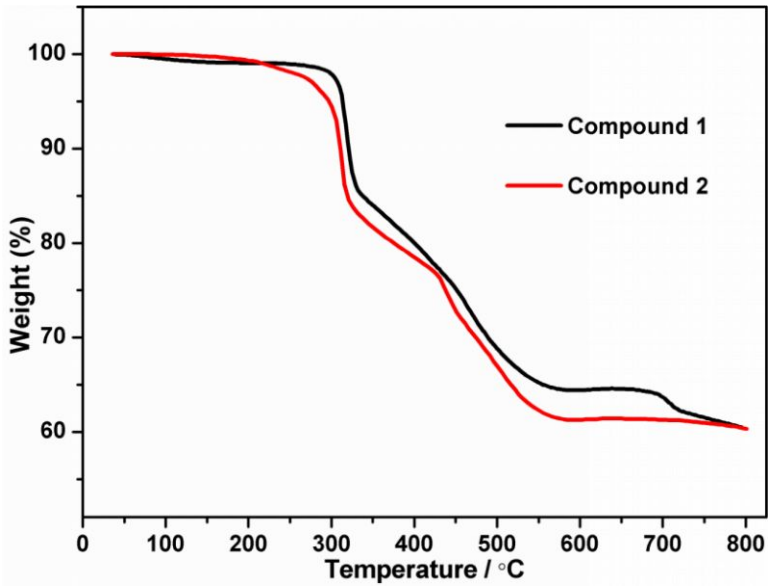

Figure S6. TGA plot of **1** and **2**.

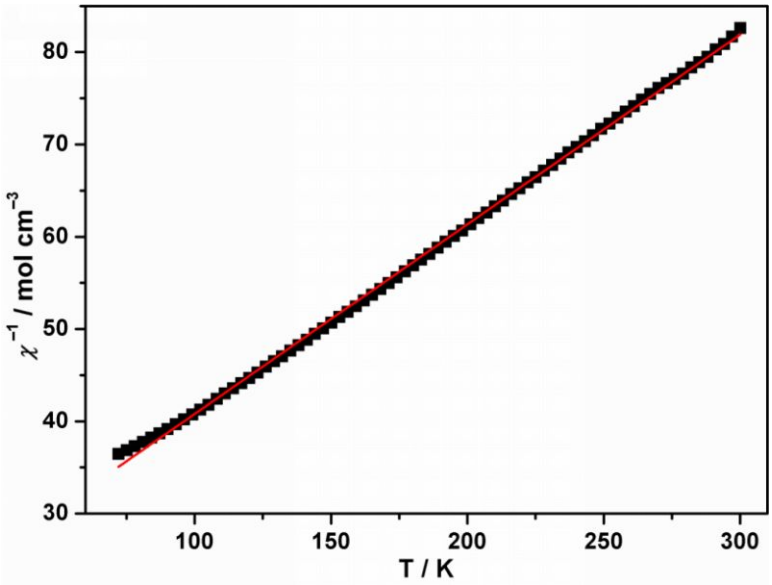

Figure S7. The χ^{-1} *vs T* plots of **1**. Solid lines represent the Curie-Weiss fitting.

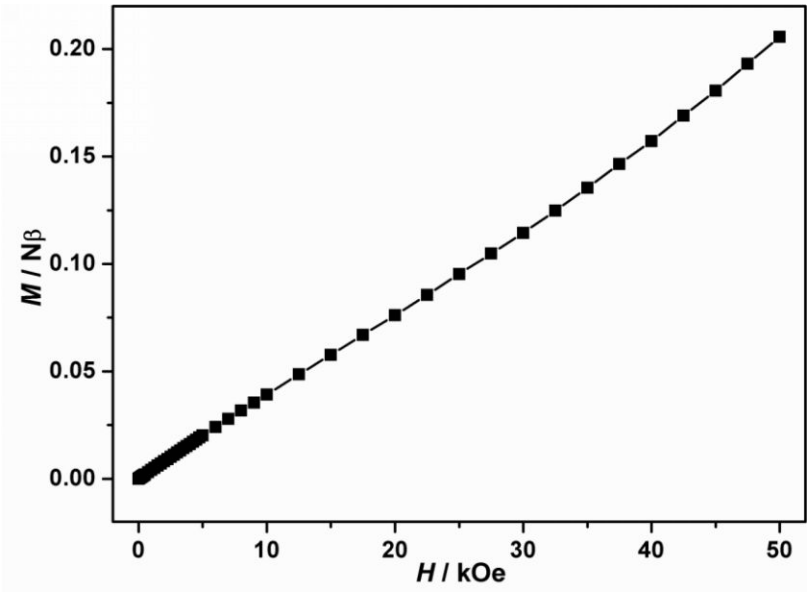

Figure S8. Isothermal magnetization curve of **1** at 2 K.

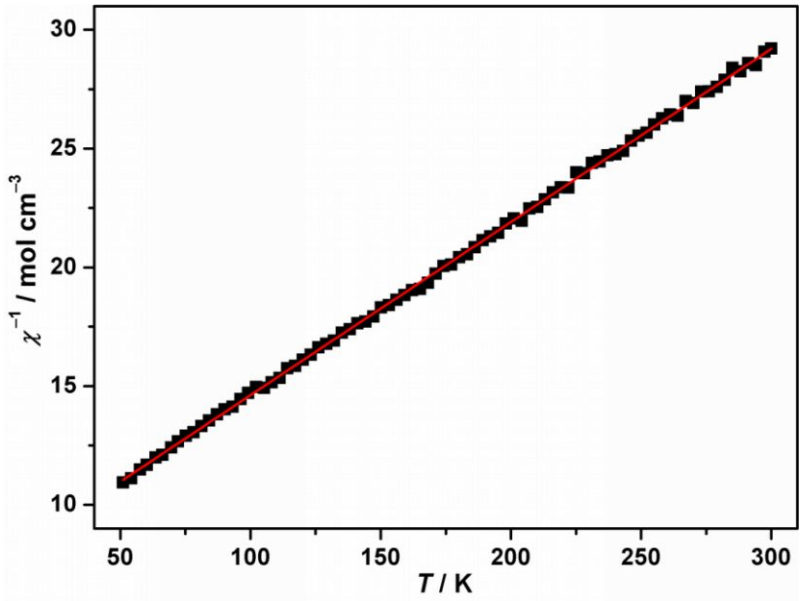

Figure S9. The χ^{-1} *vs T* plots of **2**. Solid lines represent the Curie-Weiss fitting.

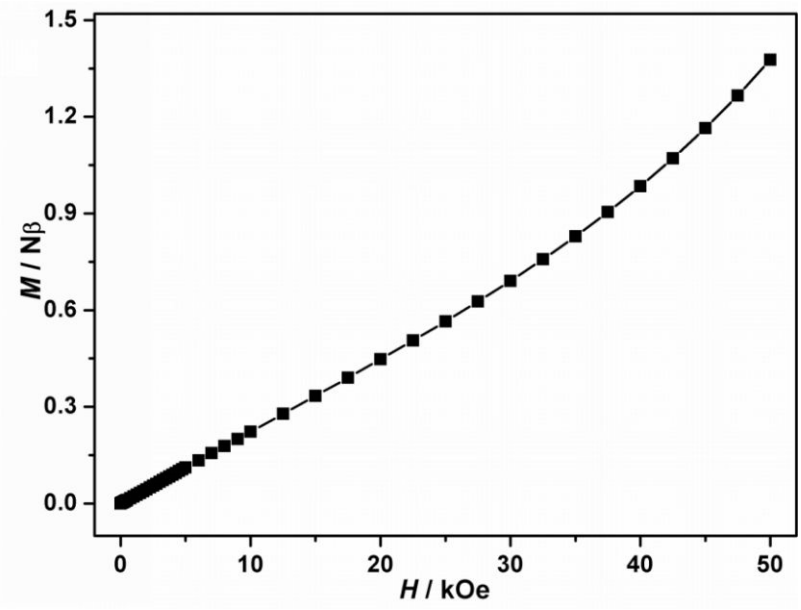

Figure S10. Isothermal magnetization curve of **2** at 2 K.

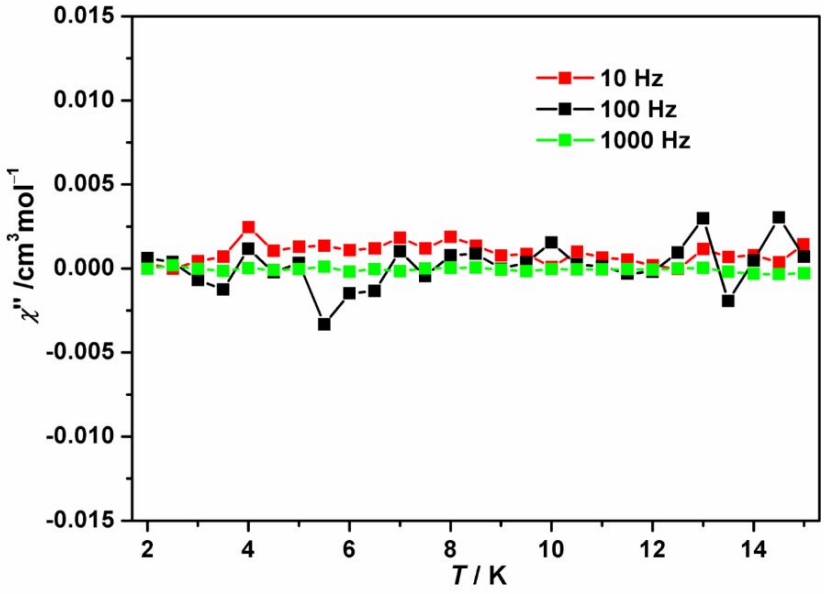

Figure S11. Temperature dependence of the out-phase components of ac magnetic susceptibility for **1** in a zero-dc and 5 Oe ac field at various ac frequencies.

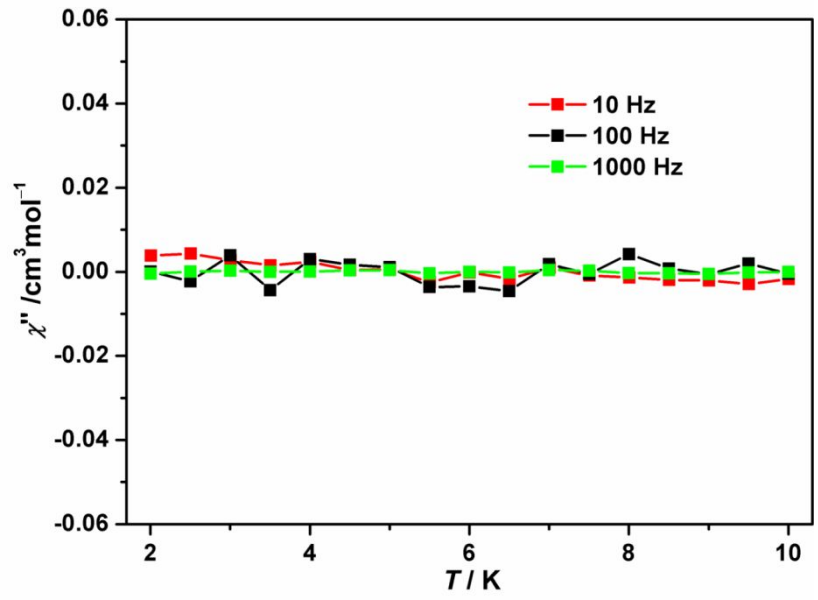

Figure S12. Temperature dependence of the out-phase components of ac magnetic susceptibility for **2** in a zero-dc and 5 Oe ac field at various ac frequencies.

Table S1. Selected bond lengths (Å) and angles (°) for **1**

Fe(1)-O(1)	1.962(5)	O(3)-P(1)	1.532(5)
Fe(1)-O(9)#1	1.971(4)	O(4)-P(2)	1.491(5)
Fe(1)-O(3)#3	1.974(5)	O(5)-P(2)	1.518(5)
Fe(1)-O(7)	1.976(4)	O(6)-P(2)	1.532(5)
Fe(1)-O(4)#3	1.992(5)	O(7)-P(3)	1.531(4)
Fe(1)-O(12)	2.027(2)	O(8)-P(3)	1.487(5)
O(1)-P(1)	1.506(5)	O(9)-P(3)	1.533(5)
O(2)-P(1)	1.507(5)		
O(1)-Fe(1)-O(9)#1	87.13(19)	O(3)#3-Fe(1)-O(12)	89.11(18)
O(1)-Fe(1)-O(3)#3	94.5(2)	O(7)-Fe(1)-O(12)	86.38(16)
O(9)#1-Fe(1)-O(3)#3	89.8(2)	O(4)#3-Fe(1)-O(12)	90.8(2)
O(1)-Fe(1)-O(7)	90.12(19)	O(1)-P(1)-O(2)	112.1(3)
O(9)#1-Fe(1)-O(7)	92.52(19)	O(1)-P(1)-O(3)	111.2(3)
O(3)#3-Fe(1)-O(7)	174.92(19)	O(2)-P(1)-O(3)	111.2(3)
O(1)-Fe(1)-O(4)#3	92.9(2)	O(4)-P(2)-O(5)	107.9(3)
O(9)#1-Fe(1)-O(4)#3	179.9(2)	O(4)-P(2)-O(6)	113.3(4)
O(3)#3-Fe(1)-O(4)#3	90.3(2)	O(5)-P(2)-O(6)	106.8(3)
O(7)-Fe(1)-O(4)#3	87.40(19)	O(8)-P(3)-O(7)	110.1(3)
O(1)-Fe(1)-O(12)	174.8(2)	O(8)-P(3)-O(9)	113.5(3)
O(9)#1-Fe(1)-O(12)	89.14(16)	O(7)-P(3)-O(9)	109.7(3)

Symmetry codes: #1: -x+2, y, -z+3/2; #2: -x+1/2, -y+3/2, -z+2; #3: -x+2, -y+1, -z+2.

Table S2. Selected bond lengths (Å) and angles (°) for **2**

O(16)-Fe(2)	1.974(4)	O(2)-P(1)	1.507(5)
O(16)-Fe(1)	2.037(4)	O(3)-P(1)	1.535(4)
Fe(1)-O(8)	2.007(4)	O(4)-P(2)	1.529(5)
Fe(1)-O(9)#1	2.031(5)	O(5)-P(2)	1.554(4)
Fe(1)-O(4)	2.034(5)	O(6)-P(2)	1.486(5)
Fe(1)-O(1)	2.048(5)	O(7)-P(3)	1.492(6)
Fe(1)-O(10)#1	2.086(5)	O(8)-P(3)	1.507(4)
Fe(2)-O(5)#2	1.987(5)	O(9)-P(3)	1.531(4)
Fe(2)-O(5)	1.987(5)	O(10)-P(4)	1.519(5)
Fe(2)-O(3)	2.005(4)	O(11)-P(4)	1.489(5)
Fe(2)-O(3)#2	2.005(4)	O(12)-P(4)	1.564(5)
O(1)-P(1)	1.523(5)		
O(8)-Fe(1)-O(9)#1	92.52(19)	O(16)#2-Fe(2)-O(3)	89.63(17)
O(8)-Fe(1)-O(4)	92.16(19)	O(16)-Fe(2)-O(3)	90.37(17)
O(9)#1-Fe(1)-O(4)	175.26(17)	O(5)#2-Fe(2)-O(3)	88.23(19)
O(8)-Fe(1)-O(16)	174.33(18)	O(5)-Fe(2)-O(3)	91.77(19)
O(9)#1-Fe(1)-O(16)	85.85(17)	O(16)#2-Fe(2)-O(3)#2	90.37(17)
O(4)-Fe(1)-O(16)	89.42(17)	O(16)-Fe(2)-O(3)#2	89.63(17)
O(8)-Fe(1)-O(1)	93.85(19)	O(5)#2-Fe(2)-O(3)#2	91.77(19)
O(9)#1-Fe(1)-O(1)	90.9(2)	O(5)-Fe(2)-O(3)#2	88.23(19)
O(4)-Fe(1)-O(1)	89.59(19)	O(3)-Fe(2)-O(3)#2	180.0
O(16)-Fe(1)-O(1)	91.61(17)	O(2)-P(1)-O(1)	112.5(3)
O(8)-Fe(1)-O(10)#1	90.2(2)	O(2)-P(1)-O(3)	111.1(3)
O(9)#1-Fe(1)-O(10)#1	88.0(2)	O(1)-P(1)-O(3)	111.5(2)
O(4)-Fe(1)-O(10)#1	91.2(2)	O(6)-P(2)-O(4)	112.1(3)
O(16)-Fe(1)-O(10)#1	84.33(18)	O(6)-P(2)-O(5)	113.0(3)
O(1)-Fe(1)-O(10)#1	175.85(18)	O(4)-P(2)-O(5)	110.4(2)

O(16)#2-Fe(2)-O(16)	180.0	O(7)-P(3)-O(8)	112.5(3)
O(16)#2-Fe(2)-O(5)#2	90.82(17)	O(7)-P(3)-O(9)	110.7(3)
O(16)-Fe(2)-O(5)#2	89.18(17)	O(8)-P(3)-O(9)	111.5(3)
O(16)#2-Fe(2)-O(5)	89.18(17)	O(11)-P(4)-O(10)	116.2(3)
O(16)-Fe(2)-O(5)	90.82(17)	O(11)-P(4)-O(12)	105.8(3)
O(5)#2-Fe(2)-O(5)	180.0	O(10)-P(4)-O(12)	110.1(3)

Symmetry codes: #1: -x+1, -y+2, -z; #2: -x+1, -y+2, -z+1.

Table S3. Details of Hydrogen Bond Interactions in **1** at 293K.

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DHA) (deg)
O13-H13...O9_$1	0.82	2.59	3.252(12)	139.4
O13-H13...O6	0.82	2.38	2.912(11)	123.7
O6-H6...O3_$3	0.84	2.02	2.819(7)	158.3
N2-H2B...O8_$4	0.89	2.61	3.191(7)	123.4
N2-H2B...O7_$4	0.89	1.98	2.831(6)	160.9
N2-H2A...O2_$5	0.89	1.84	2.717(7)	166.5
N1-H1C...O5_$8	0.89	2.11	2.975(8)	165.2
N1-H1C...O4_$8	0.89	2.63	3.287(8)	131.1
N1-H1B...O2_$7	0.89	2.05	2.801(8)	141.6
N1-H1A...O8_$6	0.89	1.76	2.592(8)	155.2

Table S4. Details of Hydrogen Bond Interactions in **2** at 293K.

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DHA) (deg)
O16-H16A...N1_$3	0.89	2.65	3.096(8)	112.4
O16-H16A...O5_$1	0.89	1.90	2.780(6)	168.1
O16-H16B...N4_$4	0.89	2.54	3.096(8)	121.4
O16-H16B...O3_$1	0.89	1.96	2.805(6)	158.7
O16-H16B...O5	0.89	2.38	2.821(6)	110.9
N1-H1A...O16_$6	0.89	2.53	3.096(8)	122.3
N1-H1A...O9_$7	0.89	2.00	2.860(7)	163.0
N1-H1B...O15_$8	0.89	1.91	2.785(10)	165.8
N1-H1C...O5_$8	0.89	1.99	2.845(8)	160.7
N2-H2D...O7	0.89	1.75	2.601(8)	160.6
N2-H2E...O4	0.89	1.97	2.819(7)	158.4
N3-H3A...O2_$5	0.89	2.03	2.901(19)	165.0
N3-H3B...O2_$6	0.89	1.83	2.709(17)	170.3
N3A-H3A1...O2_$6	0.89	1.95	2.808(13)	161.3
N3A-H3A2...O11_$6	0.89	2.10	2.932(12)	155.7
N3A-H3A2...O12_$6	0.89	2.62	3.166(12)	120.9
N4-H4D...O3_$5	0.89	1.95	2.821(8)	165.3
N4-H4E...O16_$9	0.89	2.52	3.096(8)	123.0
N4-H4E...O10_$10	0.89	1.99	2.843(7)	160.8
N4-H4F...O6_$11	0.89	1.83	2.678(8)	159.7
O12-H12...O9_$2	0.90	2.04	2.934(7)	171.1
O14-H14...O1	0.82	2.14	2.946(7)	169.9
O15-H15C...O11_$5	0.95	2.15	3.083(10)	169.4
O15-H15D...O11_$12	0.90	1.80	2.691(10)	171.0

Table S5. Continuous Shape Measure (CShM) analyses of geometries for Fe1 in compound **1** by SHAPE 2.0 Software

Geometry	**Fe**1
Hexagon (D_{6h})	31.765
Pentagonal pyramid (C_{5v})	27.955
Octahedron (O_h)	0.176
Trigonal prism (D_{3h})	15.116
Johnson pentagonal pyramid J2 (C_{5v})	31.631

Table S6. Continuous Shape Measure (CShM) analyses of geometries for Fe1 and Fe2 in compound **2** by SHAPE 2.0 Software

Geometry	**Fe**1	**Fe2**
Hexagon (D_{6h})	32.959	32.294
Pentagonal pyramid (C_{5v})	28.905	29.861
Octahedron (O_h)	0.108	0.021
Trigonal prism (D_{3h})	15.779	16.503
Johnson pentagonal pyramid J2 (C_{5v})	32.672	33.344