Electronic Supplementary Information (ESI) for

Modulation of spin transition in 2D Hofmann frameworks via $\pi\cdots\pi$ stacking between the axial 2,5-dipyridyl-1,3,4-oxadiazoles

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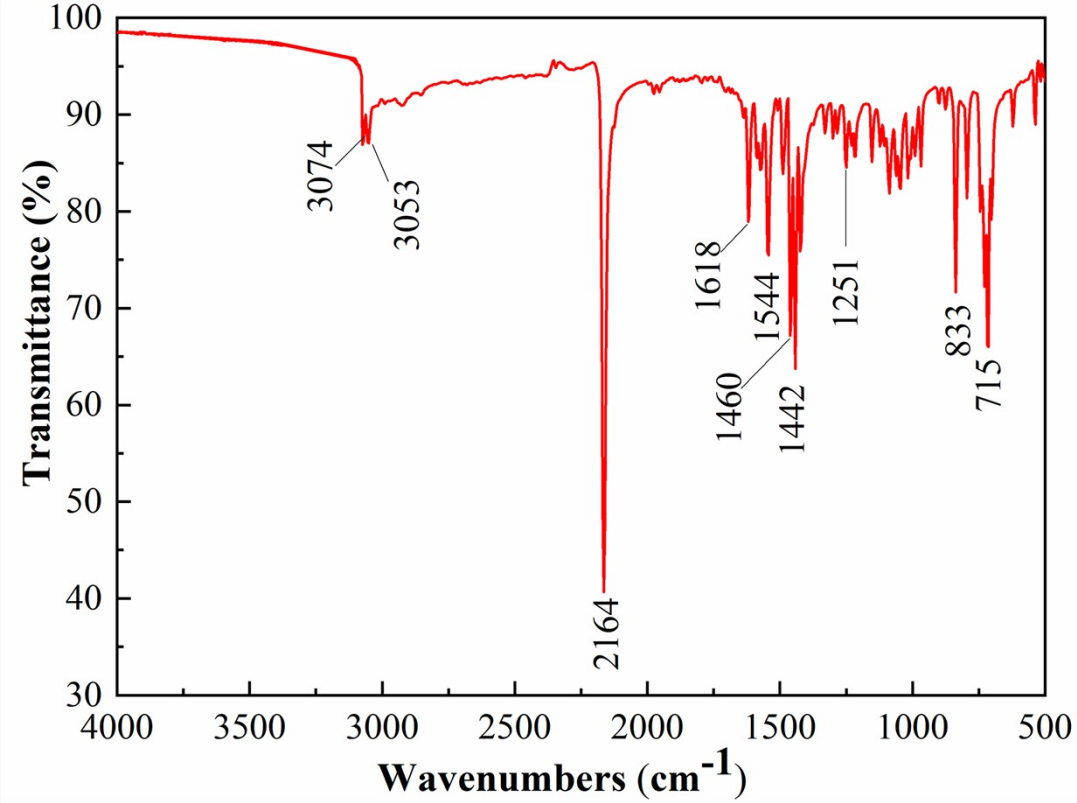

Fig. S1 The IR spectrum of **1**.

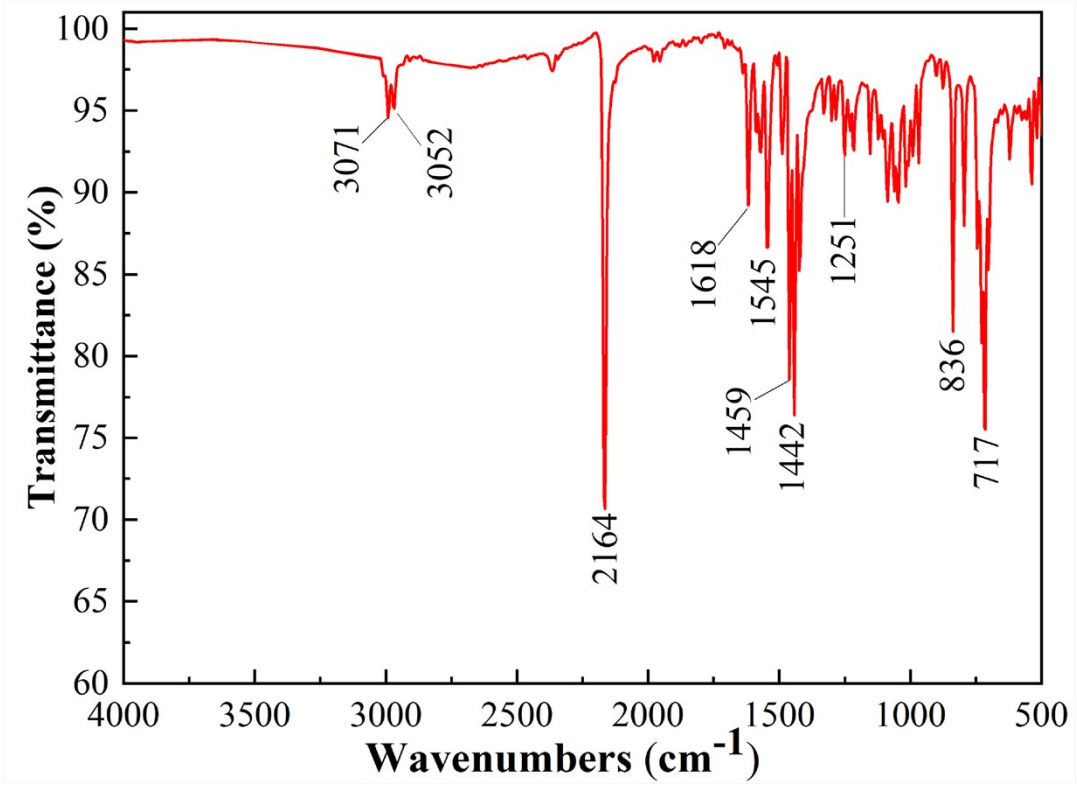

Fig. S2 The IR spectrum of **2**.

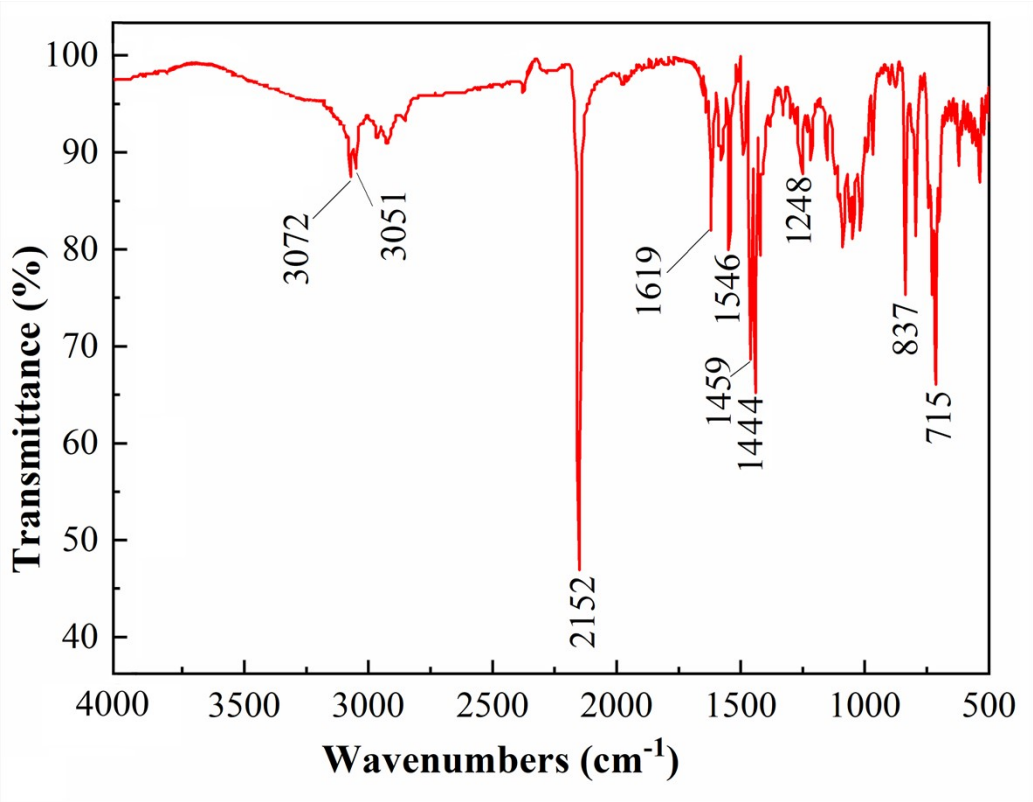

Fig. S3 The IR spectrum of **3**.

2. The thermogravimetric analysis curves of 1-3

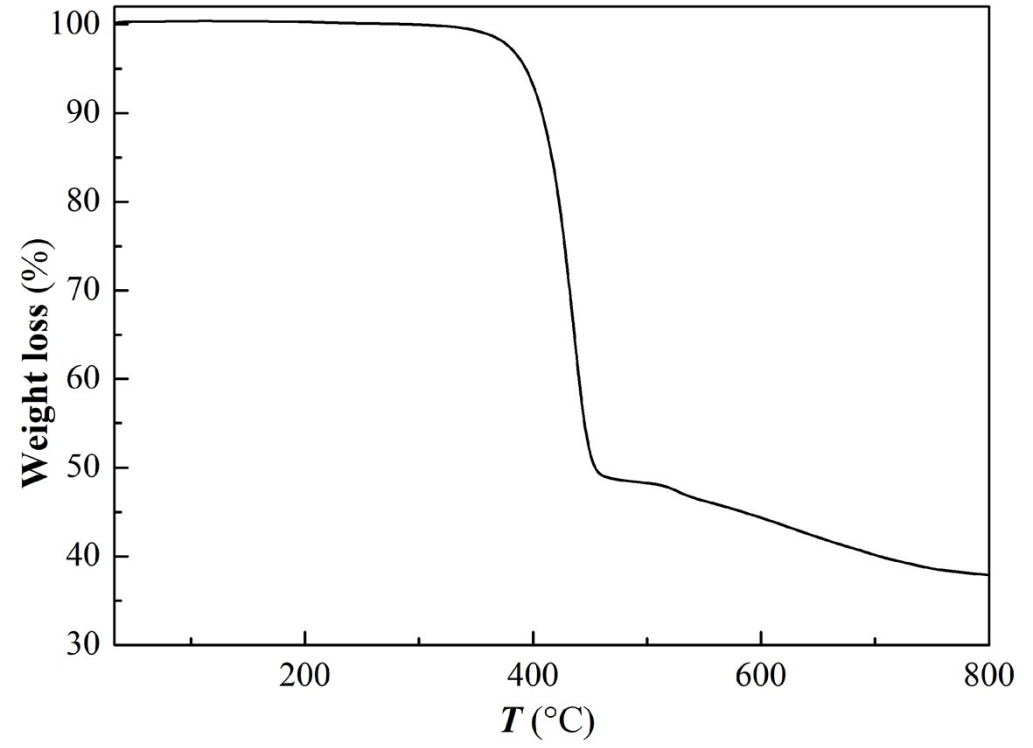

Fig. S4 Thermogravimetric analysis curve of **1**.

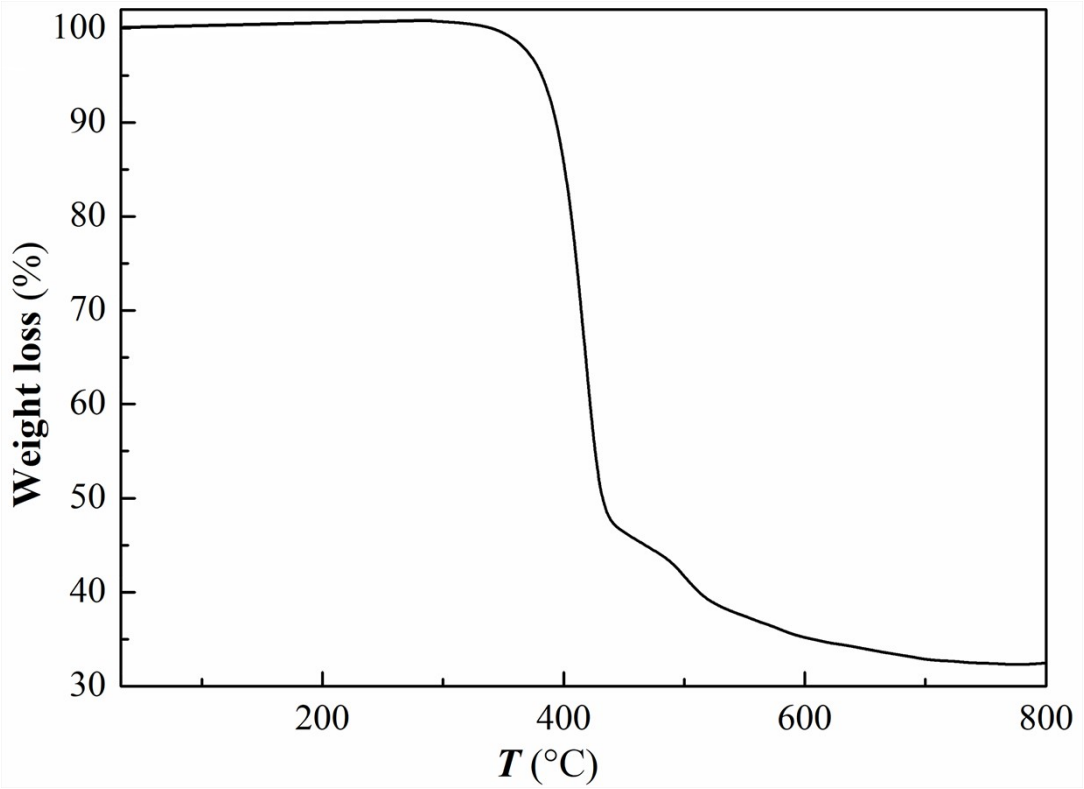

Fig. S5 Thermogravimetric analysis curve of **2**.

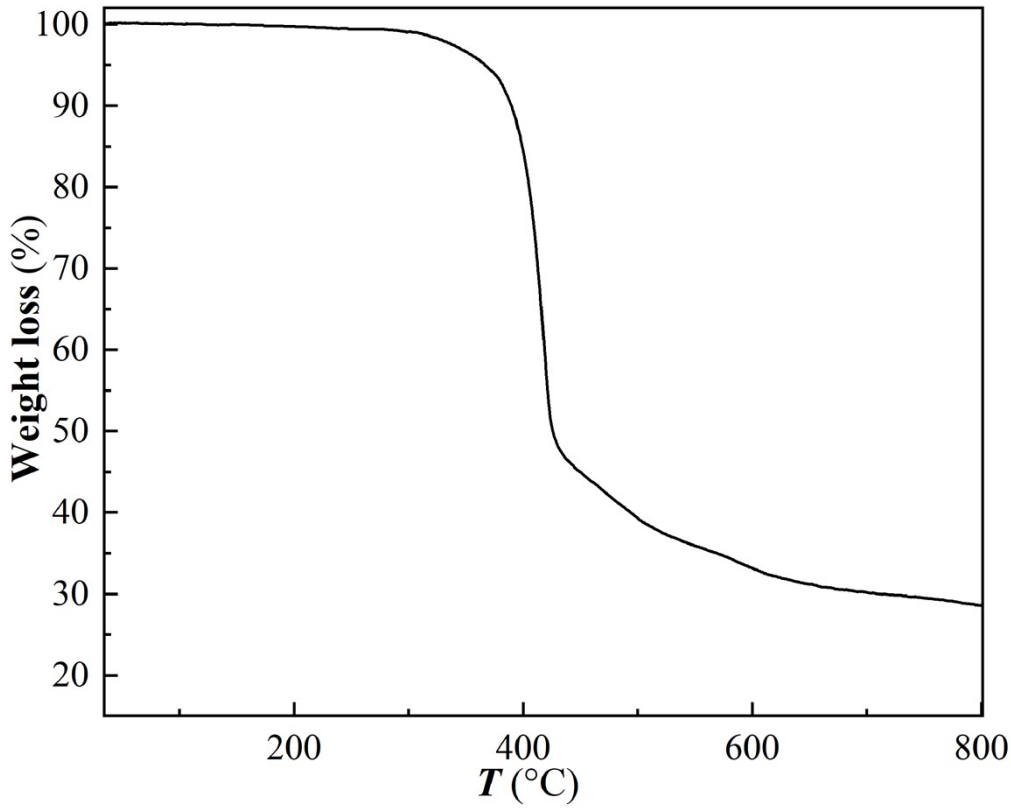

Fig. S6 Thermogravimetric analysis curve of **3**.

3. The PXRD patterns of 1-3

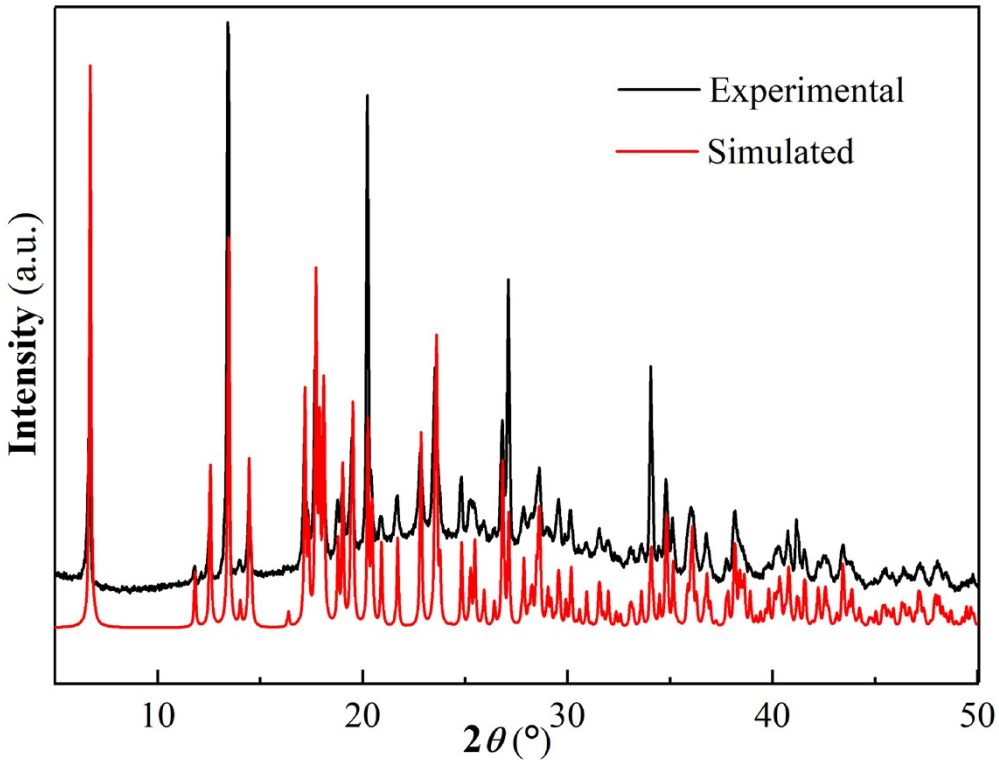

Fig. S7 The PXRD patterns of **1**.

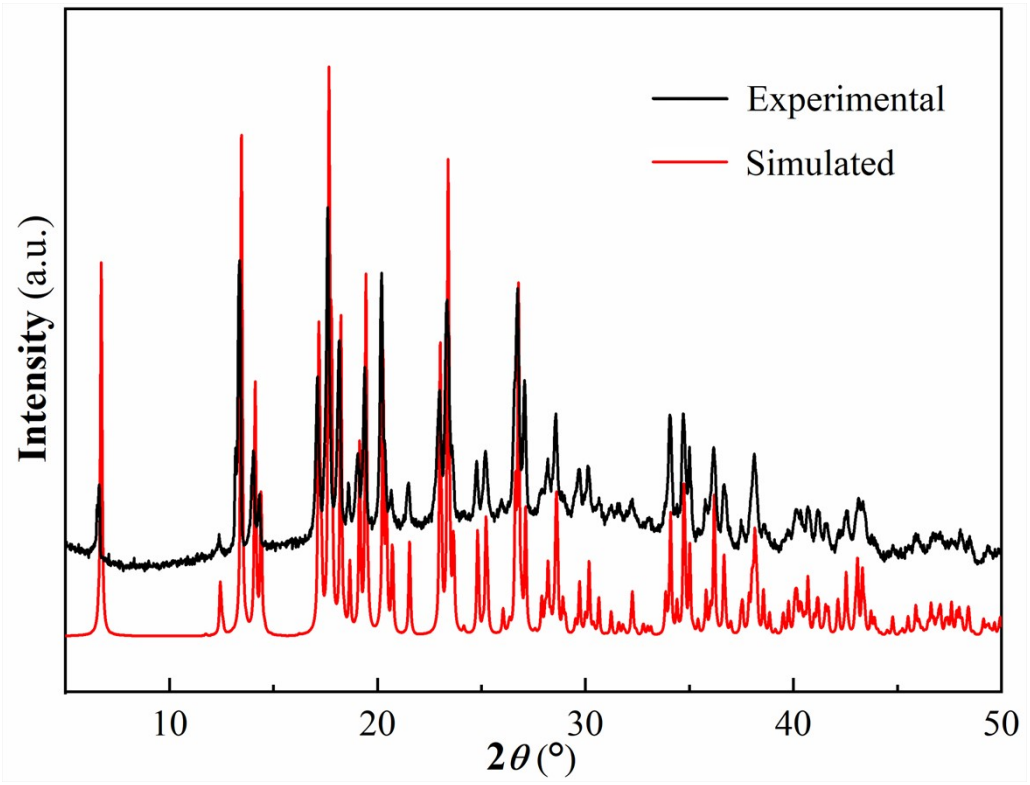

Fig. S8 The PXRD patterns of **2**.

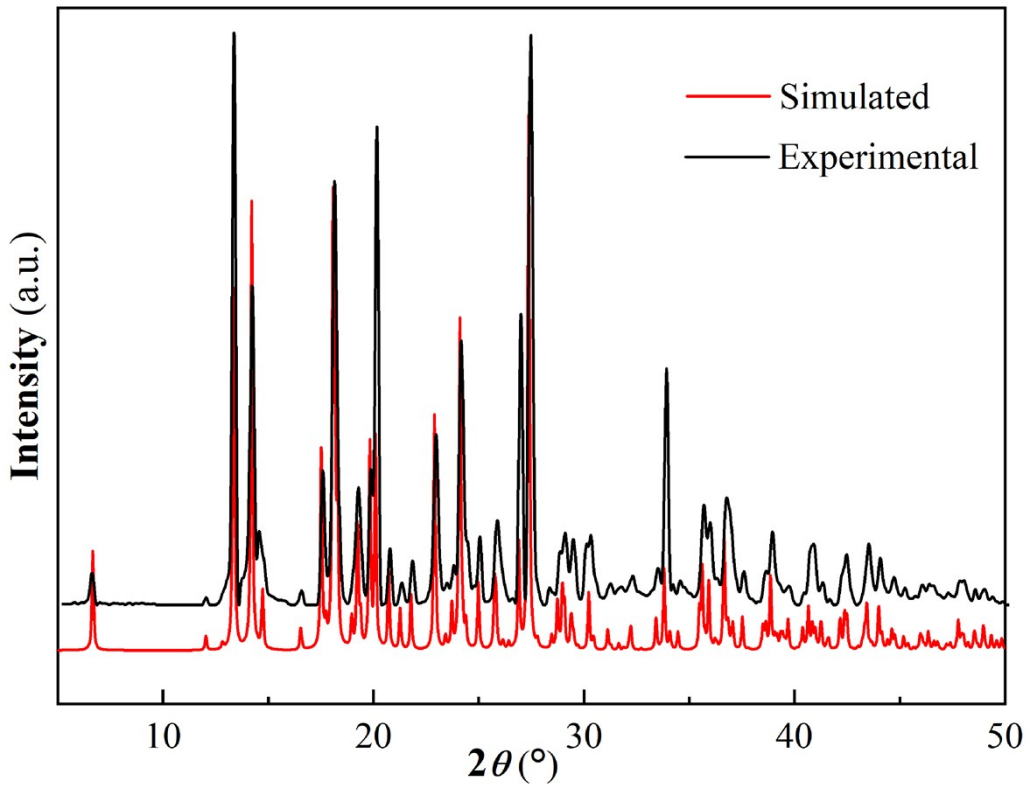

Fig. S9 The PXRD patterns of **3**.

4. Molecular Structures of 1-3

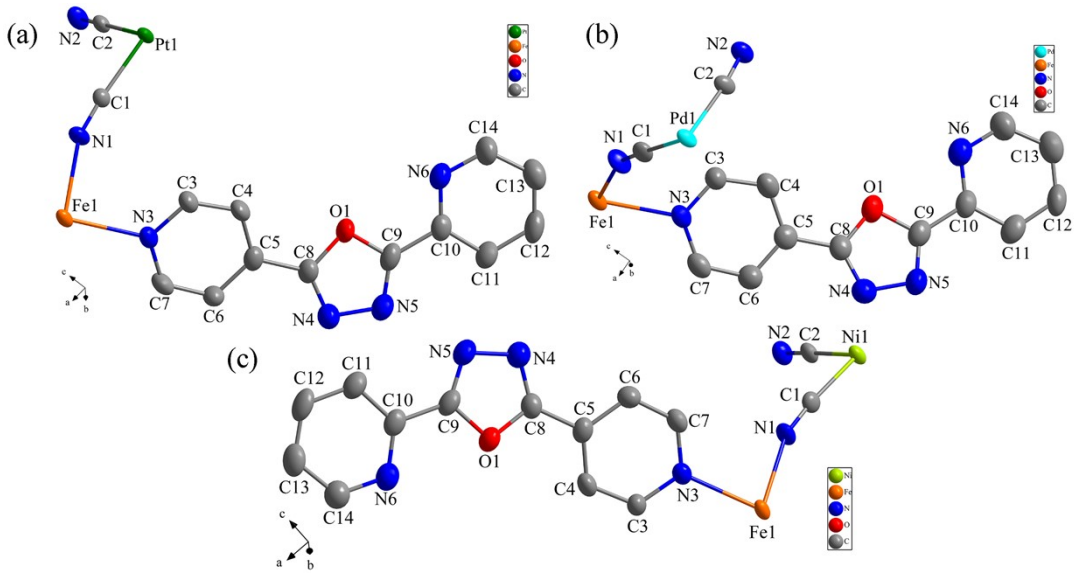

Fig. S10 The asymmetric unit of **1** (a), **2** (b) and **3** (c) with 50% thermal ellipsoids probability, all hydrogen atoms are omitted for clarity.

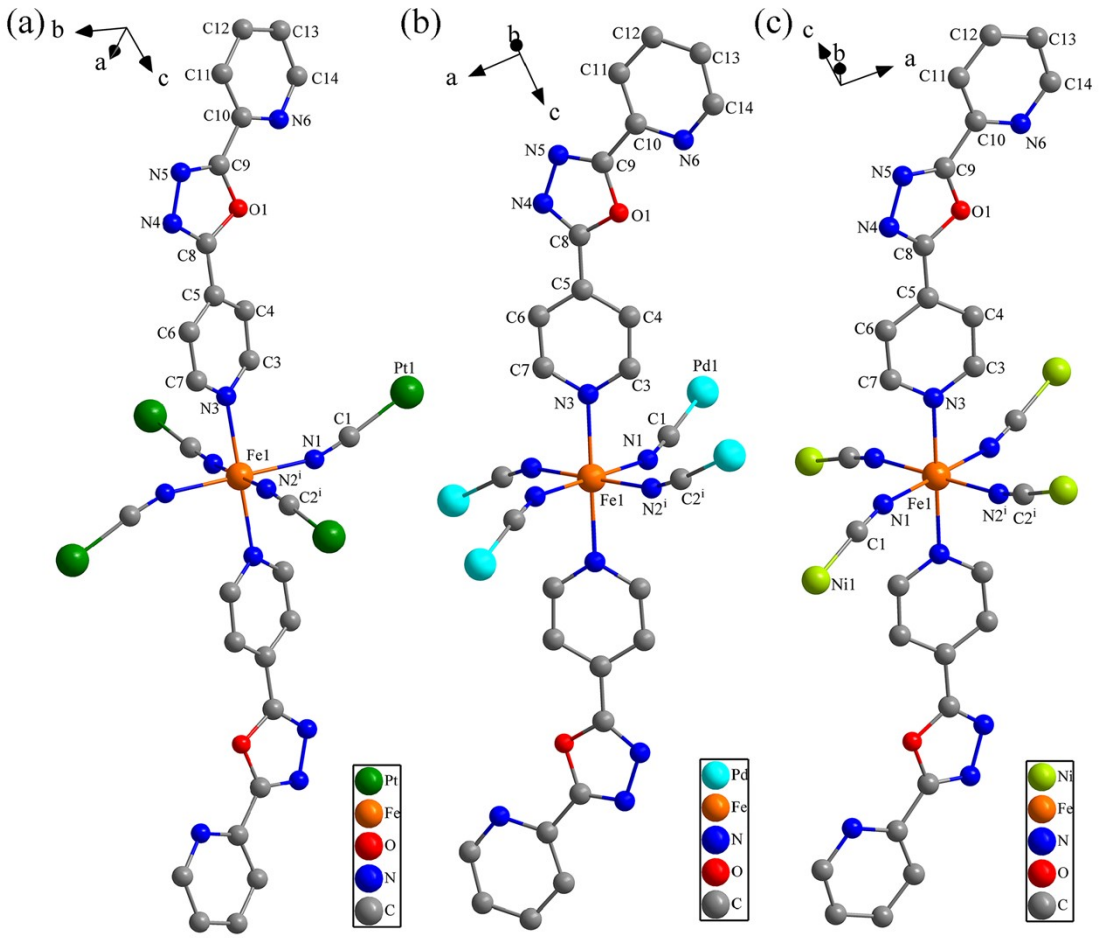

Fig. S11 The coordinated environments of Fe^{2+} ion in **1** (a), **2** (b) and **3** (c), all hydrogen atoms are omitted for clarity.

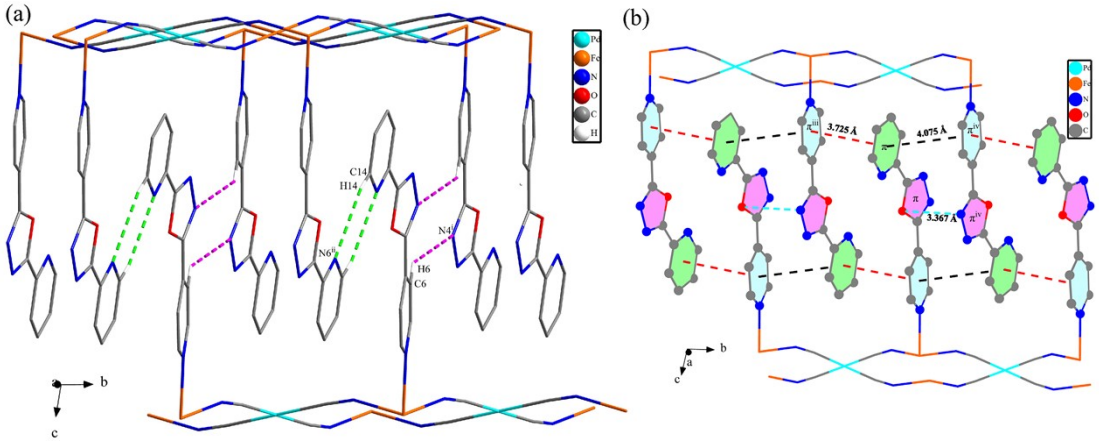

Fig. S12 (a) Two kinds of intermolecular hydrogen bonds in **2**; (b) Three kinds of offset face-to-face $\pi\cdots\pi$ interactions in **2**.

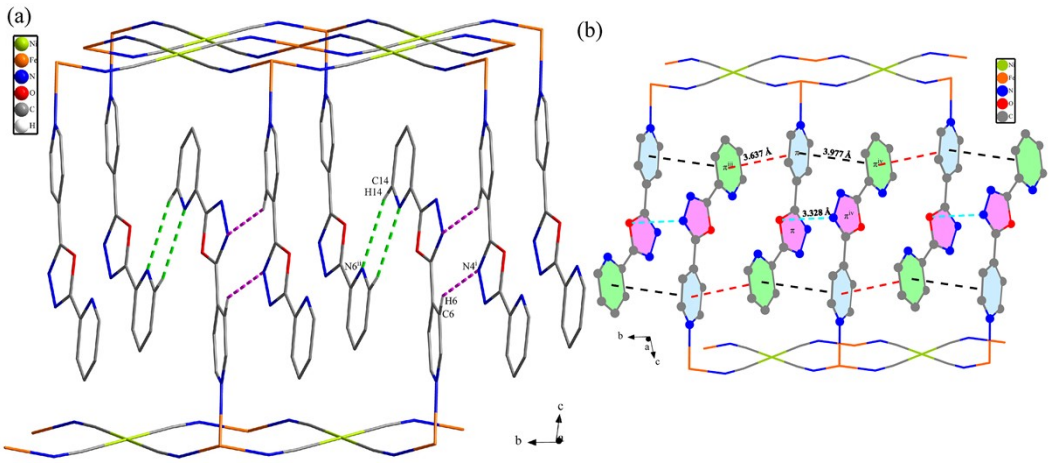

Fig. S13 (a) Two kinds of intermolecular hydrogen bonds in **3**; (b) Three kinds of offset face-to-face $\pi\cdots\pi$ interactions in **3**.

5. Selected bond distances and angles for 1-3

Table S1 Selected bond distances (Å) and angles (°) for **1-3**

1		**2**		**3**	
Fe1-N1	2.140(4)	Fe1-N1	2.171(5)	Fe1-N1	2.148(3)
Fe1-N2^{i}	2.157(4)	Fe1-N2^{i}	2.157(5)	Fe1-N2^{i}	2.165(3)
Fe1-N3	2.214(4)	Fe1-N3	2.226(5)	Fe1-N3	2.212(3)
Pt1-C1	1.986(5)	Pd1-C1	1.995(6)	Ni1-C1	1.861(3)
Pt1-C2	1.986(5)	Pd1-C2	1.999(6)	Ni1-C2	1.869(3)
C1-N1	1.144(6)	C1-N1	1.140(8)	C1-N1	1.144(4)
N2-C2	1.142(6)	N2-C2	1.139(8)	N2-C2	1.134(4)
Fe$\cdots$Fe^{iv}	10.334(2)	Fe$\cdots$Fe^{iv}	10.400(3)	Fe$\cdots$Fe^{iv}	10.116(2)
N1-Fe1-N2^{i}	88.88(16)	N1-Fe1-N2^{i}	91.47(2)	N1-Fe1-N2^{i}	88.58(10)
N1-Fe1-N2^{ii}	91.12(16)	N1-Fe1-N2^{ii}	88.53(2)	N1-Fe1-N2^{ii}	91.42(10)
N2^{i}-Fe1-N3	91.83(15)	N2^{i}-Fe1-N3	89.71(4)	N2^{i}-Fe1-N3	87.67(10)
N2^{i}-Fe1-N3^{iii}	88.17(15)	N2^{i}-Fe1-N3^{iii}	90.30(6)	N2^{i}-Fe1-N3^{iii}	92.33(10)
N1-Fe1-N3	89.83(15)	N1-Fe1-N3	88.31(5)	N1-Fe1-N3	90.46(10)
N1-Fe1-N3^{iii}	90.17(15)	N1-Fe1-N3^{iii}	91.70(5)	N1-Fe1-N3^{iii}	89.54(10)
C1-N1-Fe1	160.17(1)	C1-N1-Fe1	158.93(4)	C1-N1-Fe1	161.23(3)
C2^{i}-N2^{i}-Fe1	159.52(1)	C2^{i}-N2^{i}-Fe1	160.56(8)	C2^{i}-N2^{i}-Fe1	161.32(3)
C7-N3-Fe1	122.17(6)	C7-N3-Fe1	121.30(11)	C7-N3-Fe1	121.50(2)
C3-N3-Fe1	121.61(9)	C3-N3-Fe1	121.57(4)	C3-N3-Fe1	121.29(2)
N1-C1-Pt1	175.30(1)	N1-C1-Pd1	176.65(3)	N1-C1-Ni1	174.75(3)
N2-C2-Pt1	176.97(5)	N2-C2-Pd1	174.20(8)	N2-C2-Ni1	176.08(3)

Symmetry codes: **1**: i) 2-*x*, 1-*y*, 2-*z*; ii) *x*, 1+*y*, *z*; iii) 2-*x*, 2-*y*, 2-*z*; iv) *x*-1, *y*-1, *z*; **2**: i) 1-*x*, 1-*y*, 2-*z*; ii) 1+*x*, *y*, *z*; iii) 2-*x*, 1-*y*, 2-*z*; iv) *x*-1, 1+*y*, *z*; **3**: i) -*x*, -*y*, -*z*; ii) *x*, 1+*y*, *z*; iii) -*x*, 1-*y*, -*z*; iv) *x*-1, *y*-1, *z*.

Table S2 Dihedral angles (°) for complexes **1-3**

Complex	4-Py/Ox	2-Py/Ox	$[FeN_4]/[M(CN)_4]^{2-}$
1	14.7(4)	6.5(2)	33.0(3)
2	15.3(5)	5.6(2)	34.7(2)
3	15.1(2)	7.3(3)	32.2(2)

Table S3 Critical temperature ($T_{1/2}$), hysteresis width (ΔT), interlayer distance (D_L), cent···cent (D_C) and plane···plane (D_P) distances of $\pi\cdots\pi$ interactions and dihedral angles of three 2D Hofmann SCO frameworks

Complex	Size of ligand (Å)	$T_{1/2}$ (K)	ΔT (K)	D_L (Å)	D_C (Å)	4-Py/ 2-Py (°)	D_P (Å)	$[FeN_4]/[Pt(CN)_4]^{2-}$ (°)
$[Fe(2,4\text{-}Bipy)_2Pt(CN)_4]$	7.958(2)	206/247	41	11.576(2)	4.055(4)	0	3.780(2)	44.3(2)
$[Fe(ppe)_2Pt(CN)_4]$	10.293(4)	132/136	4	–	–	–	–	–
$[Fe(ppo)_2Pt(CN)_4]$	11.463(4)	94	0	13.137(4)	3.703(3)/ 4.046(4)	8.96	–	33.0(3)