Supporting information for

Mononuclear high spin Fe(III) complexes: synthesis, crystal structures, magnetic and optical properties

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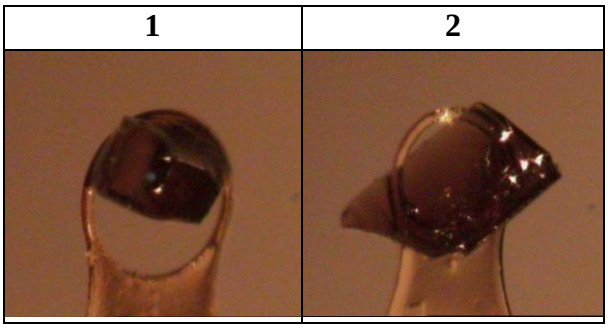


Fig. S1 Photographs of crystals' compound **1** and **2** selected for the single crystal X-ray experiment

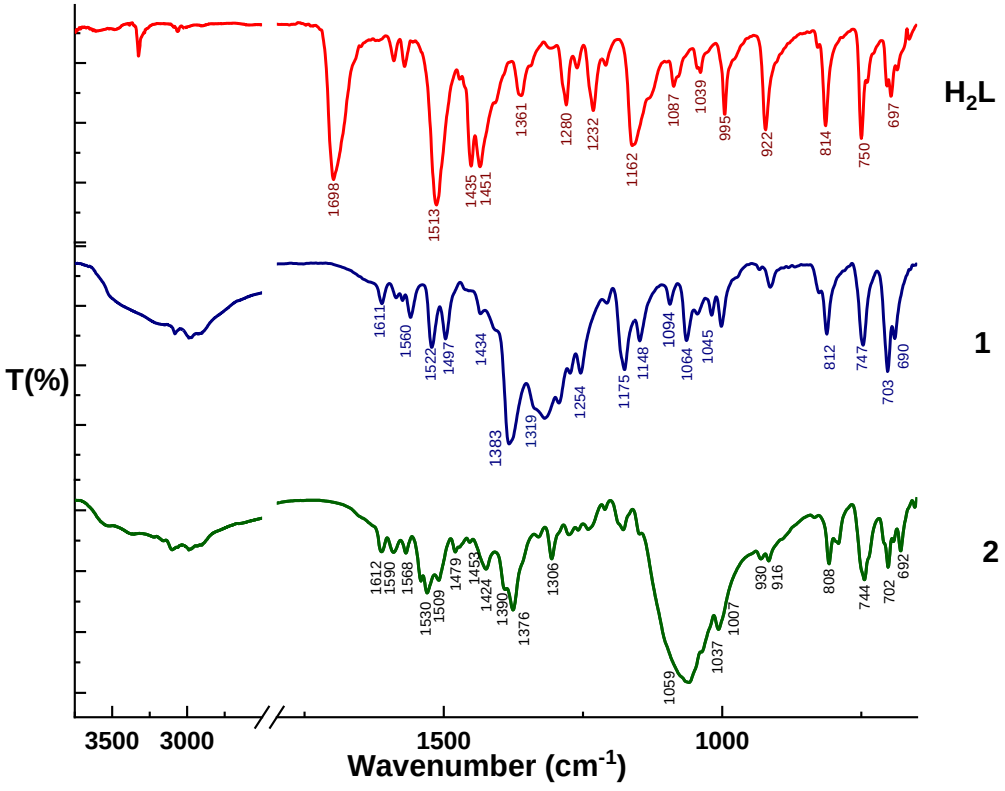


Fig. S2 The IR spectra of compounds **1, 2** and H_2L Schiff base ligand

Table S1. Selected bond lengths (Å) and angles (°) in coordination metal environment in **1** and **2**

	1	**2**	
		A	B
Bonds	(Å)	(Å)	(Å)
Fe(1)-O(1W)/O(3W)	2.040(2)	2.035(4)	2.200(4)
Fe(1)-O(2W)/O(4W)	1.995(2)	2.007(4)	2.035(4)
Fe(1)-O(1)	2.071(2)	2.061(4)	2.066(3)
Fe(1)-O(2)	2.085(2)	2.073(3)	2.072(4)
Fe(1)-N(3)	2.186(2)	2.192(4)	2.185(5)
Fe(1)-N(4)	2.197(2)	2.200(4)	2.197(4)
Fe(1)-N(5)	2.186(2)	2.189(4)	2.188(4)
Angles	(°)	(°)	(°)
O(1*w*)/O(3*w*)-Fe(1)-O(2*w*)/O(4*w*)	176.31(8)	179.29(17)	177.76(16)
O(1*w*)/O(3*w*)-Fe(1)-O(1)	91.11(8)	88.27(16)	91.71(16)
O(1*w*)/(3*w*)-Fe(1)-O(2)	89.52(8)	90.12(17)	92.40(16)
O(1*w*)/(3*w*)-Fe(1)-N(3)	88.47(8)	90.94(18)	89.35(17)
O(1*w*)/(3*w*)-Fe(1)-N(4)	88.04(8)	88.87(16)	89.21(17)
O(1*w*)/(3*w*)-Fe(1)-N(5)	89.17(8)	89.40(17)	89.72(17)
O(2*w*)/(4*w*)-Fe(1)-O(1)	91.67(8)	91.70(16)	89.36(16)
O(2*w*)/(4*w*)-Fe(1)-O(2)	93.50(8)	90.56(16)	89.75(17)
O(2*w*)/(4*w*)-Fe(1)-N(3)	90.08(8)	88.37(17)	89.12(18)
O(2*w*)/(4*w*)-Fe(1)-N(4)	88.28(8)	90.71(16)	88.73(16)
O(2*w*)/(4*w*)-Fe(1)-N(5)	89.74(8)	91.00(17)	90.38(18)
O(1)-Fe(1)-O(2)	75.89(7)	76.68(13)	77.00(14)
O(1)-Fe(1)-N(3)	72.09(8)	71.84(15)	71.84(15)
O(1)-Fe(1)-N(4)	141.85(8)	141.66(15)	141.34(16)
O(1)-Fe(1)-N(5)	148.23(8)	148.58(15)	148.64(16)
O(2)-Fe(1)-N(3)	147.87(8)	148.45(16)	148.83(16)
O(2)-Fe(1)-N(4)	142.20(8)	141.56(15)	141.56(16)
O(2)-Fe(1)-N(5)	72.34(8)	72.00(15)	71.64(15)
N(3)-Fe(1)-N(4)	69.76(8)	69.99(16)	69.55(16)
N(3)-Fe(1)-N(5)	139.66(8)	139.54(17)	139.51(17)
N(4)-Fe(1)-N(5)	69.91(8)	69.57(16)	69.96(17)

Table S2. Hydrogen bond distances (Å) and angles (°) in **1** and **2**

D-H···A	*d*(H···A)	*d*(D···A)	∠(DHA)	Symmetry transformations for acceptor
1				
N(1)-H(1)···O(8)	2.10	2.828(4)	162	*x*, *y*, *z*
N(7)-H(2)···O(9)	1.98	2.802(3)	159	-*x*+1, -*y*+2, -*z*+2
O(1*w*)-H(1*w*)···O(2)	2.07	2.883(3)	159	-*x*+1, -*y*+2, -*z*+1
O(1*w*)-H(2*w*)···O(3)	2.08	2.710(4)	130	-*x*+1, -*y*+1, -*z*+1
O(2*w*)-H(1*w*)···O(7)	1.88	2.713(3)	166	-*x*+1, -*y*+1, -*z*+1
O(2*w*)-H(2*w*)···O(3)	1.73	2.622(3)	173	-*x*+1, -*y*+1, -*z*+1
C(2)-H(2)···O(6)	2.47	3.187(5)	134	*x*, *y*, *z*
C(2)-H(2)···O(5*w*)	2.62	3.329(7)	133	-*x*, -*y*+1, -*z*+1
C(5)-H(5)···O(3)	2.53	3.268(4)	137	*x*, *y*+1, *z*
C(9)-H(9)···O(4)	2.34	3.242(4)	164	*x*+1, *y*, *z*
C(11)-H(11)···O(4)	2.53	3.292(4)	139	*x*+1, *y*, *z*
C(16)-H(16)···O(7)	2.54	3.219(4)	130	*x*, *y*+1, *z*+1
C(16)-H(16)···O(11)	2.45	3.148(5)	132	-*x*+1, -*y*+2, -*z*+2
C(17)-H(17)···O(4*w*)	2.58	3.362(5)	143	*x*, *y*+1, *z*
C(20)-H(20A)···O(8)	2.40	3.349(4)	171	*x*, *y*, *z*
C(21)-H(21B)···O(5*w*)	2.51	3.394(6)	153	-*x*+1, -*y*+1, -*z*+2
C(21)-H(21C)···O(9)	2.40	3.358(4)	174	-*x*+1, -*y*+2, -*z*+2
O(3*w*)-H(1)···O(4)	1.96	2.782(3)	162	*x*+1, *y*, *z*
O(3*w*)-H(2)···O(10)	1.99	2.823(4)	168	-*x*+1, -*y*+1, -*z*+1
O(3*w*)-H(2)···O(11)	2.50	2.945(4)	113	-*x*+1, -*y*+1, -*z*+1
O(4*w*)-H(1)···O(6)	1.79	2.755(3)	167	*x*, *y*, *z*+1
O(4*w*)-H(2)···O(3*w*)	2.00	2.866(4)	155	-*x*+1, -*y*+1, -*z*+1
O(5*w*)-H(1)···O(4*w*)	1.96	2.801(7)	158	*x*, *y*, *z*
O(5*w*)-H(1)···O(5*w*)	2.57	2.977(12)	109	-*x*, -*y*+1, -*z*+2
O(5*w*)-H(2)···O(4*w*)	2.00	3.128(7)	164	-*x*, -*y*+1, -*z*+2

2				
N(1A)-H(1)...O(20)	2.42	3.261(10)	166	-*x*+2, -*y*+1, -*z*+1
N(7A)-H(7)...O(20)	2.16	2.988(8)	160	-*x*+2, -*y*+1, -*z*+1
C(4A)-H(4)...O(13)	2.52	3.369(13)	152	-*x*+2, -*y*+1, -*z*+1
C(9A)-H(9)...O(11)	2.49	3.340(9)	152	-*x*+1, -*y*+1, -*z*+1
C(11A)-H(11)...O(22)	2.65	3.177(10)	117	*x*, *y*, *z*
C(16A)-H(16)...O(19)	2.52	3.202(15)	130	-*x*+2, -*y*+1, -*z*+1
C(17A)-H(17)...O(16)	2.47	3.339(13)	155	-*x*+2, -*y*+1, -*z*
C(20A)-H(20A)...N(2B)	2.72	3.466(9)	135	-*x*+1, -*y*+1, -*z*
O(1*w*)-H(1*w*)...O(3)	2.05	2.891(12)	170	*x*, *y*, *z*
O(1*w*)-H(2w)...O(7*w*)	2.06	2.644(7)	125	*x*, *y*, *z*
O(2*w*)-H(1*w*)...O(8*w*)	1.75	2.591(7)	163	*x*, *y*, *z*
O(2*w*)-H(2w)...O(12*w*)	1.79	2.588(8)	151	*x*, *y*, *z*
N(1B)-H(1)...O(24)	2.31	3.140(9)	163	*x*+1, *y*, *z*
N(7)-H(7)...O(24)	2.30	3.130(9)	163	*x*+1, *y*, *z*
C(3B)-H(3)...O(23)	2.50	3.226(11)	135	*x*+1, *y*, *z*
C(11B)-H(11)...O(15)	2.57	3.413(14)	151	-*x*+1, -*y*+2, -*z*+1
C(16B)-H(11)...O(22)	2.42	3.179(13)	139	*x*+1, *y*, *z*
C(20)-H(20F)...N(2A)	2.56	3.394(8)	146	-*x*+1, -*y*+1, -*z*+1
O(3*w*)-H(1*w*)...O(9*w*)	2.16	2.589(8)	111	*x*, *y*+1, *z*
O(3*w*)-H(2*w*)...O(11*w*)	1.98	2.584(9)	127	*x*, *y*, *z*
O(4*w*)-H(1w)...O(6)	2.26	2.936(11)	136	*x*, *y*, *z*
O(4*w*)-H(2*w*)...O(10*w*)	1.97	2.603(8)	130	*x*, *y*, *z*
O(5*w*)-H(1*w*)...O(11*w*)	1.69	2.42(2)	144	*x*, *y*-1, *z*
O(5*w*)-H(2*w*)...O(11*w*)	2.37	3.04(2)	137	-*x*+1, -*y*+1, -*z*+1
O(5*w*)-H(2*w*)...N(6B)	2.59	3.15(2)	125	-*x*+1, -*y*+1, -*z*+1
O(6*w*)-H(1*w*)...O(6*w*)	2.57	3.38(2)	144	*x*, *y*, *z*
O(6*w*)-H(2*w*)...N(6A)	2.32	3.15(2)	137	-*x*+1, -*y*+1, -*z*
O(7*w*)-H(1*w*)...O(1*w*)	1.85	2.644(7)	175	*x*, *y*, *z*
O(7*w*)-H(2*w*)...O(15A)	2.43	3.14(2)	173	*x*, *y*-1, *z*
O(8*w*)-H(1*w*)...O(5)	2.38	3.01(1)	131	*x*, *y*, *z*
O(8*w*)-H(2*w*)...O(12)	2.42	2.96(2)	122	*x*, *y*, *z*
O(9*w*)-H(1*w*)...O(4)	2.56	3.10(2)	123	*x*, *y*, *z*
O(9*w*)-H(2*w*)...O(19)	2.34	2.94(2)	128	*x*, *y*-1, *z*-1
O(10*w*)-H(1*w*)...O(24)	2.24	3.19(1)	176	*x*+1, *y*, *z*
O(10*w*)-H(2*w*)...O(12)	2.24	3.19(2)	176	*x*, *y*, *z*
O(11*w*)-H(1*w*)...O(3*w*)	1.76	2.584(9)	162	*x*, *y*, *z*
O(11*w*)-H(2*w*)...O(16)	2.28	2.94(2)	135	*x*, *y*, *z*
O(11*w*)-H(2*w*)...O(5*w*)	2.42	3.04(2)	130	-*x*+1, -*y*+1, -*z*+1
O(12*w*)-H(1*w*)...O(23)	2.09	2.96(1)	175	-*x*+1, -*y*+1, -*z*
O(12*w*)-H(2*w*)...O(6*w*)	1.85	2.65(1)	174	*x*, *y*, *z*

Table S3. Geometrical parameters for Cl–O···π interactions

Cl–O···π interactions	**d, Å**
Cl(1)–O(1)···Cg(N4A/C8A-C12A)	3.601
Cl(1)–O(2)···Cg(N4B/C8B-C12B)	3.187
Cl(1)–O(3)···Cg(N4A/C8A-C12A)	3.388
Cl(1)–O(4)···Cg(N4A/C8A-C12A)	3.875
Cl(2)–O(5)···Cg(N4B/C8B-C12B)	3.786
Cl(2)–O(6)···Cg(N4B/C8B-C12B)	3.340
Cl(2)–O(7)···Cg(N4B/C8B-C12B)	3.592
Cl(2)–O(8)···Cg(N4A/C8A-C12A)	3.143
Cl(3)–O(10)···Cg(N1A/C2A-C6A)	3.293
Cl(3)–O(11)···Cg(N7B/C15B-C19B)	3.202
Cl(3)–O(12)···Cg(N7B/C15B-C19B)	3.820
Cl(4)–O(14)···Cg(N7B/C15B-C19B)	3.315
Cl(4)–O(15)···Cg(N1A/C2A-C6A)	3.323
Cl(5)–O(17)···Cg(N1B/C2B-C6B)	3.793
Cl(5)–O(20)···Cg(N1B/C2B-C6B)	3.338

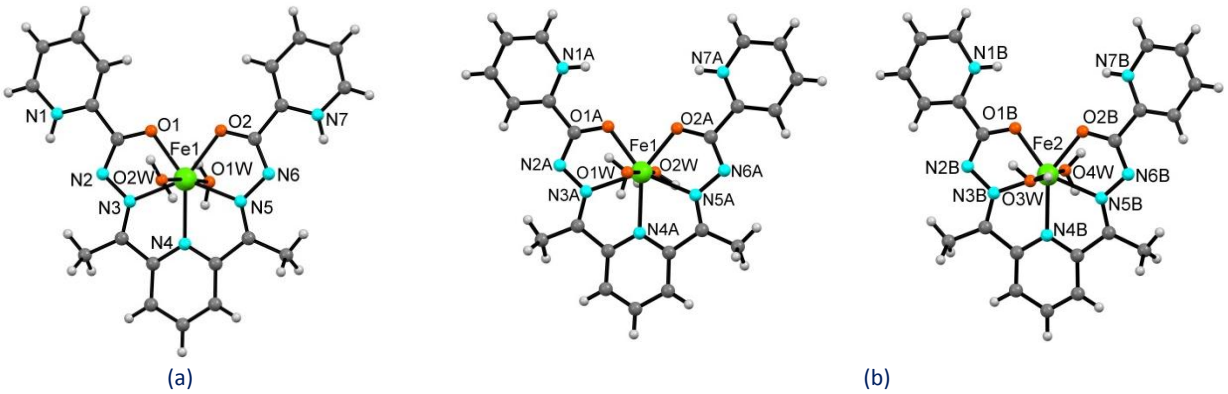


Fig. S3 Coordination geometry of Fe(III) ion in **1** and **2** with partial atom labelling

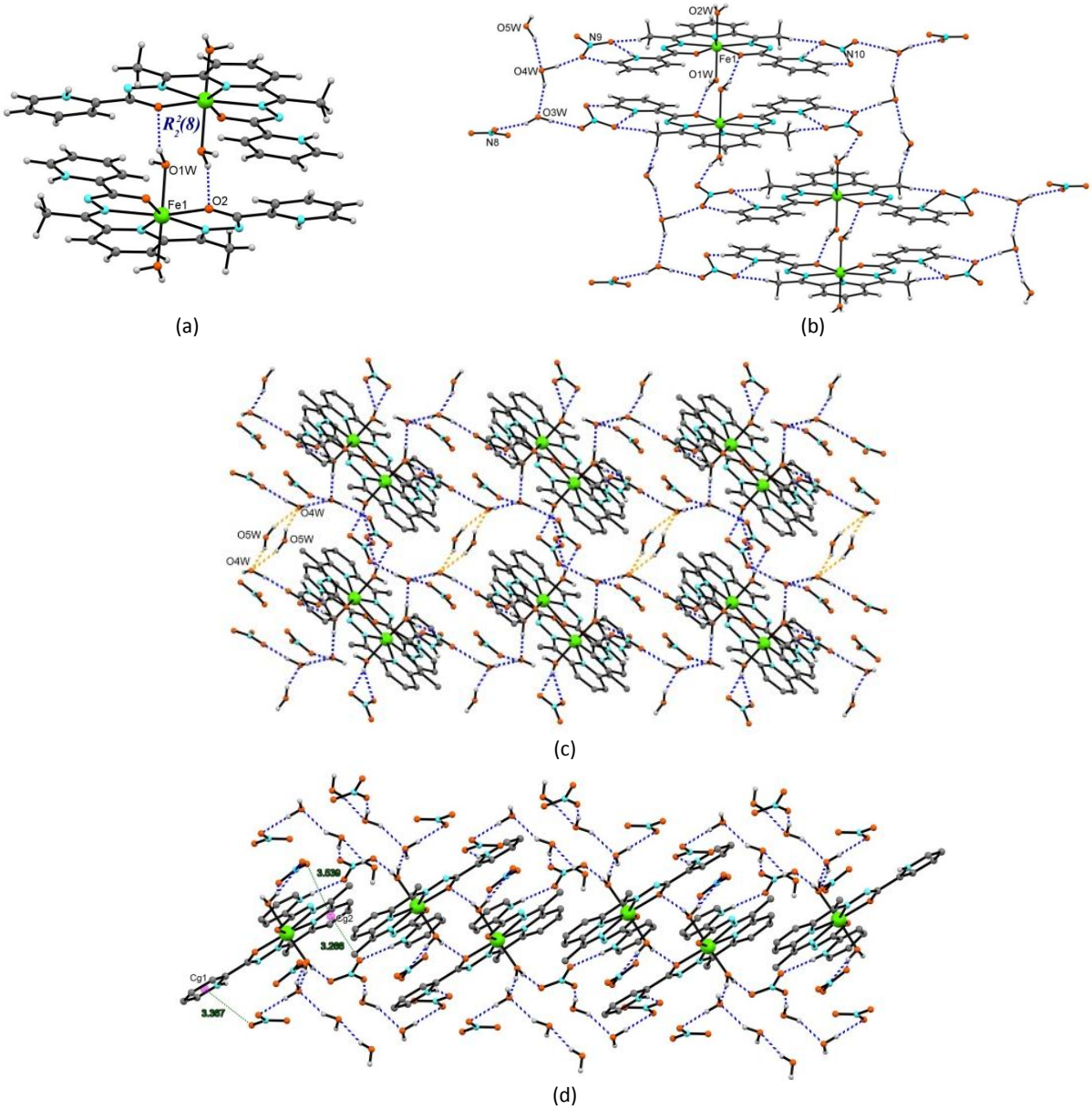
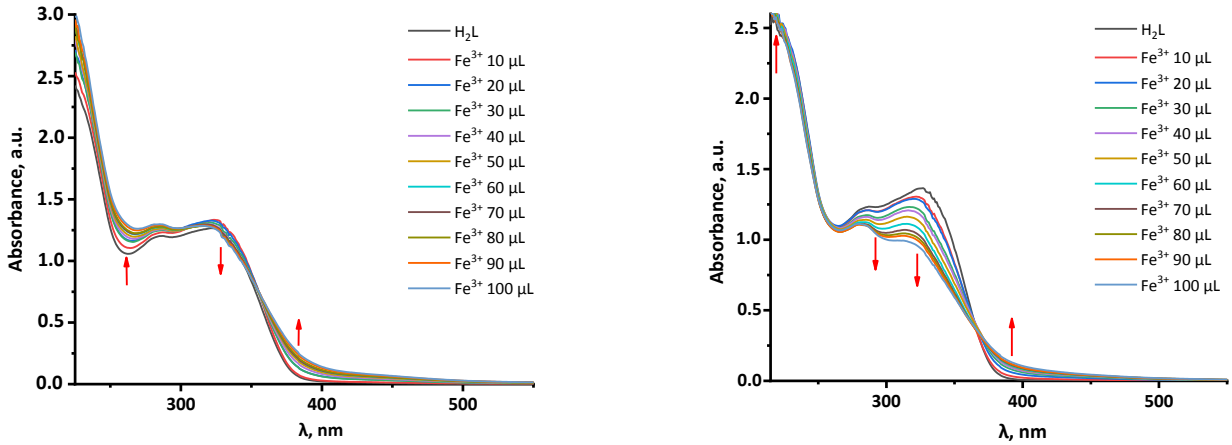


Fig. S4 Formation dimers in **1** (a); Fragments of crystal packing of **1** (b, c);
Anion···π interactions in **1**. Due to center of symmetry in the crystal the outer-sphere water molecules O4W and O5W form the four-membered rings (d).



(a) (b)

Fig. S5 UV-visible study of H_2L ligand titration profiles with varying concentration of Fe^{3+} ions from 10 to 100 µL: $Fe(NO_3)_3$ (*a*) and $Fe(ClO_4)_3$ (*b*) solutions.

Table S4. The total energies (A.U.) for different spin multiplicities calculated at different levels of theory within the DFT methodology.

Multiplicity	**2**	**4**	**6**
Functional/basis set	**Energies**		
pbe/6-31g(d,p)	-2759.09469704	-2759.0934954	-2759.11071133
B3LYP/6-31g(d,p)	-2761.08519188	-2761.07977425	-2761.1200379
B3LYP/6-311++g(2d,2p)	-2761.58332054	-2761.57514421	-2761.61250484

Table S5. Frontier orbital energies and percentage composition of molecular orbitals (MO) computed for studied cation. The MOs consist of the following fragments: iron ion, 2,6-diacetylpyridine (A) and two picolinoylhydrazones (B1 and B2).

Alpha	**Energy, eV**	**Fe (%)**	**A (%)**	**B1 (%)**	**B2 (%)**
L+4	-2.43	0	16	34	50
L+2	-3.15	1	38	23	38
L+1	-3.71	0	28	45	26
LUMO	-3.88	1	45	18	35
HOMO	-7.35	1	49	30	20
H-1	-7.75	1	36	26	36
Beta					
L+4	-3.51	16	9	38	37
L+2	-3.85	2	44	27	27
HOMO	-7.4	6	43	32	18
H-1	-7.7	4	36	22	38

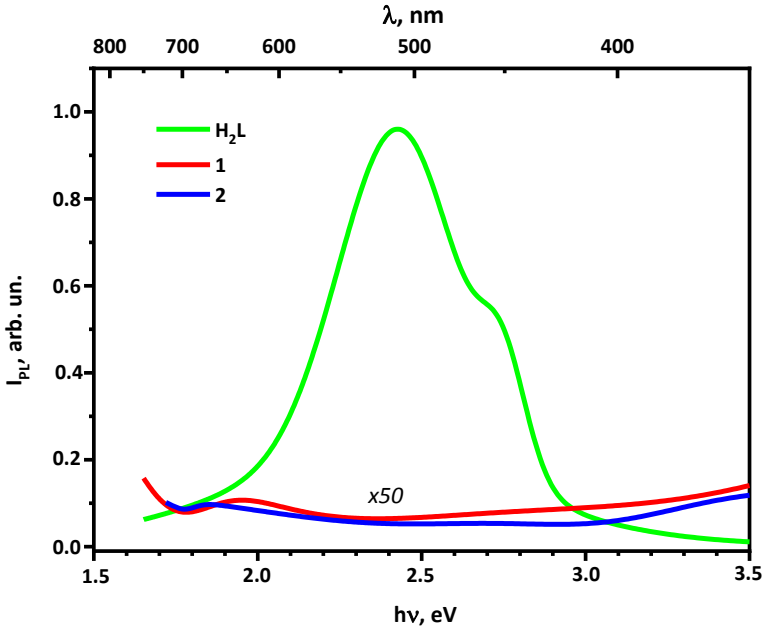
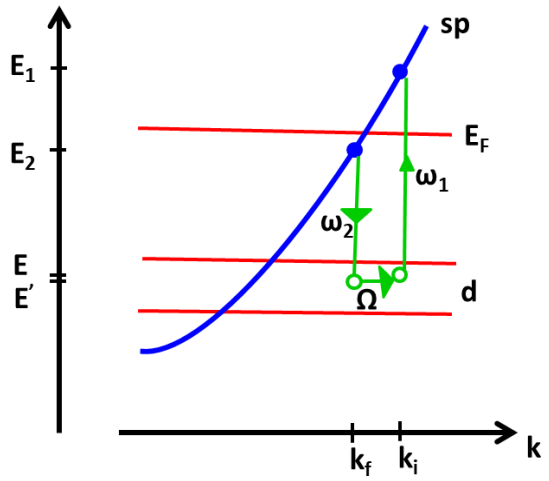


Fig. S6 Comparison of solid-state PL emission spectra for complexes **1**, **2** and coordination agent



Scheme S1. Schematic picture of the luminescence taken from [~~57~~ 58]. A photon of energy $\hbar\omega_1$, promotes an electron from the filled (narrow) *d*-band to above the Fermi level E_F (*sp*-band). The hole relaxes in momentum space by e.g., absorbing *(E > E')* or emitting *(E < E')* phonon and is eventually filled by an electron from the filled *sp*-band emitting photon of energy $\hbar\omega_2$, which is the luminescence photon.