Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information for *Thermally-induced spin-crossover in the Fe(3-Ethynylpyridine)$_2$[M(CN)$_4$] series with M = Ni, Pd, and Pt. Role of the electron density found at the CN 5σ orbital*, by R. Terrero, Y. Avila, R. Mojica, A. Cano, M. Gonzalez, M. Avila, and E. Reguera

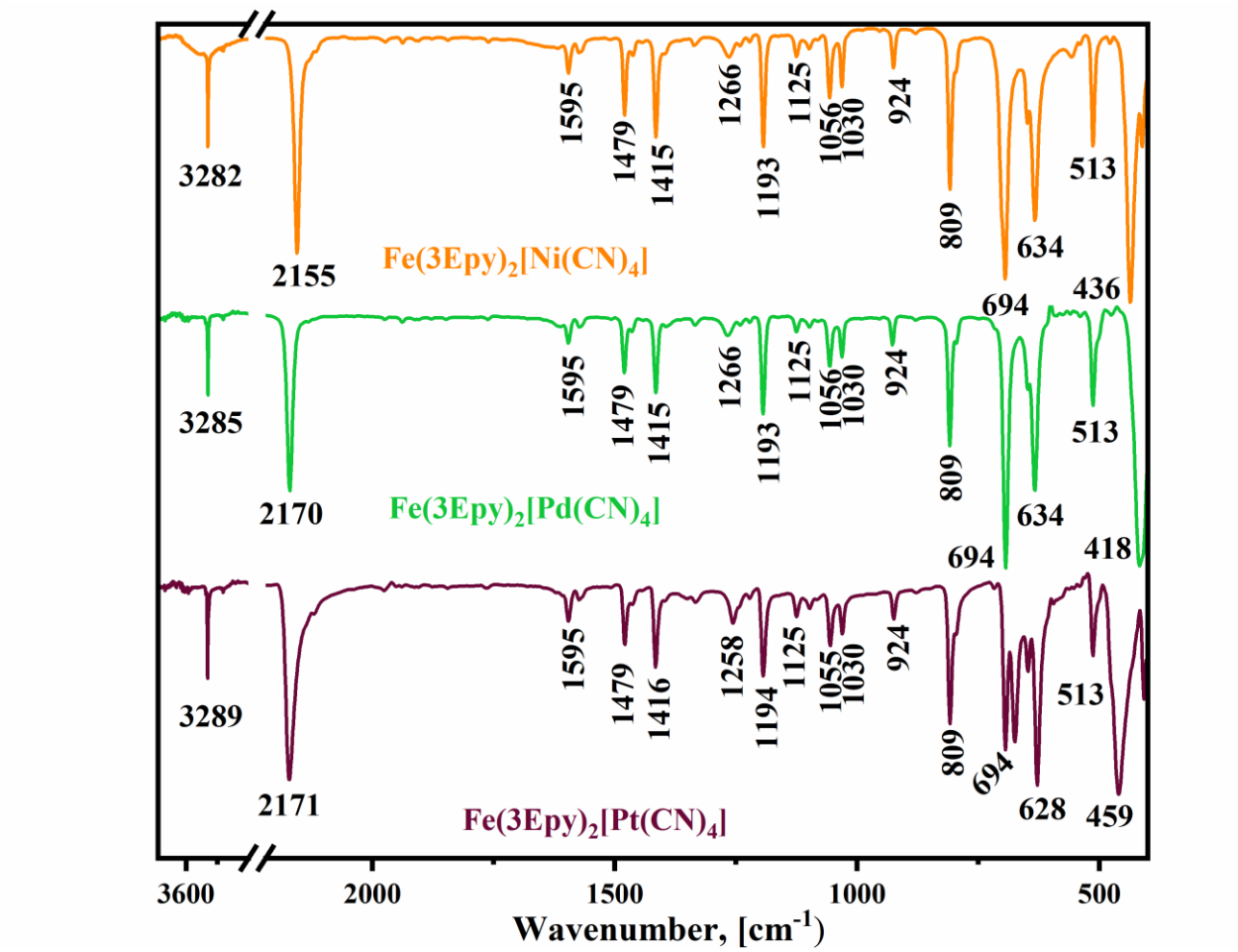

Figure S1. IR spectra at 300 K for the Fe(3-Ethynylpyridine)$_2$[M(CN)$_4$] series with M = Ni, Pd, and Pt

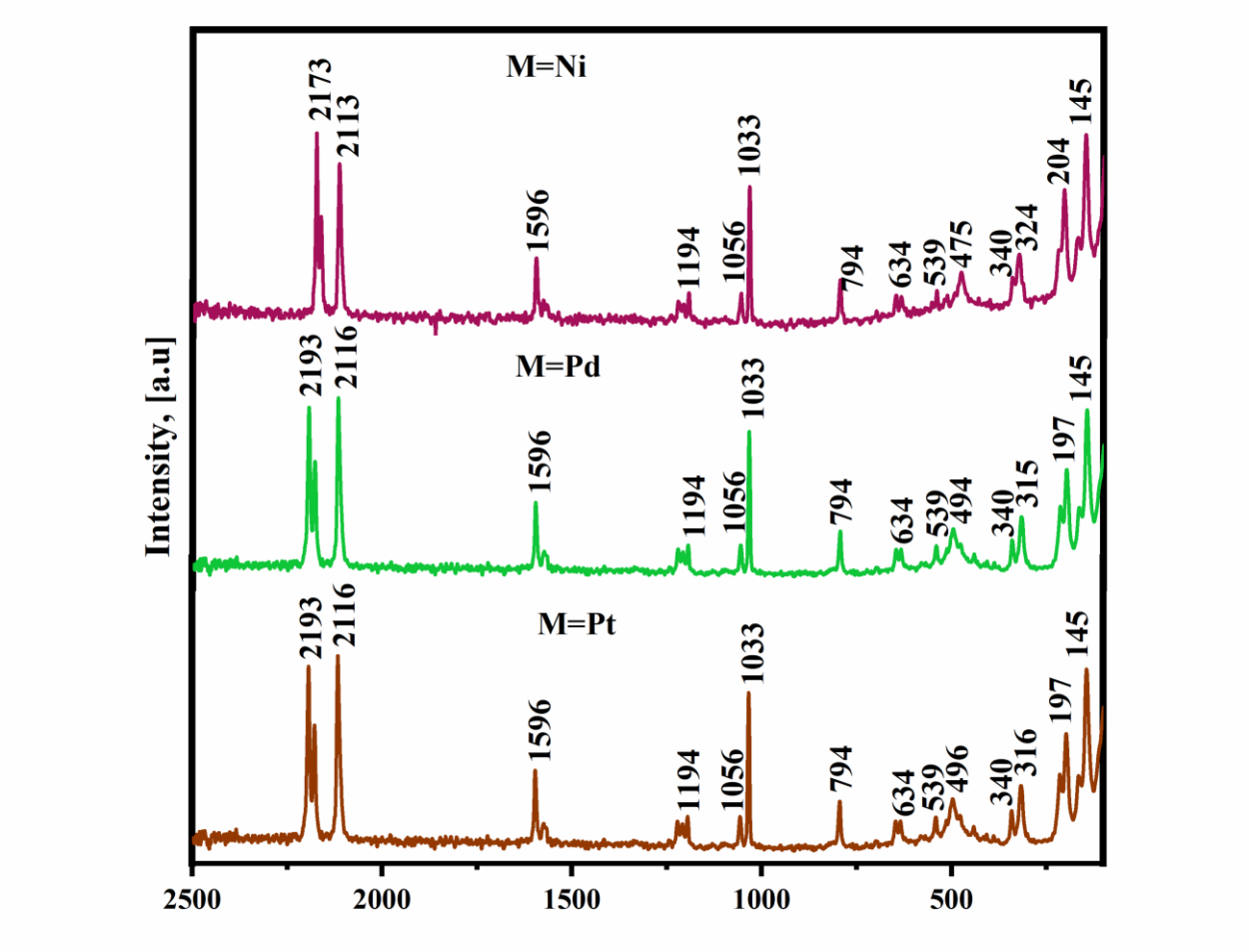

Figure S2: Raman spectra for the Fe(3-Ethynylpyridine)$_2$[M(CN)$_4$] series with M = Ni, Pd, and Pt at 300 K.

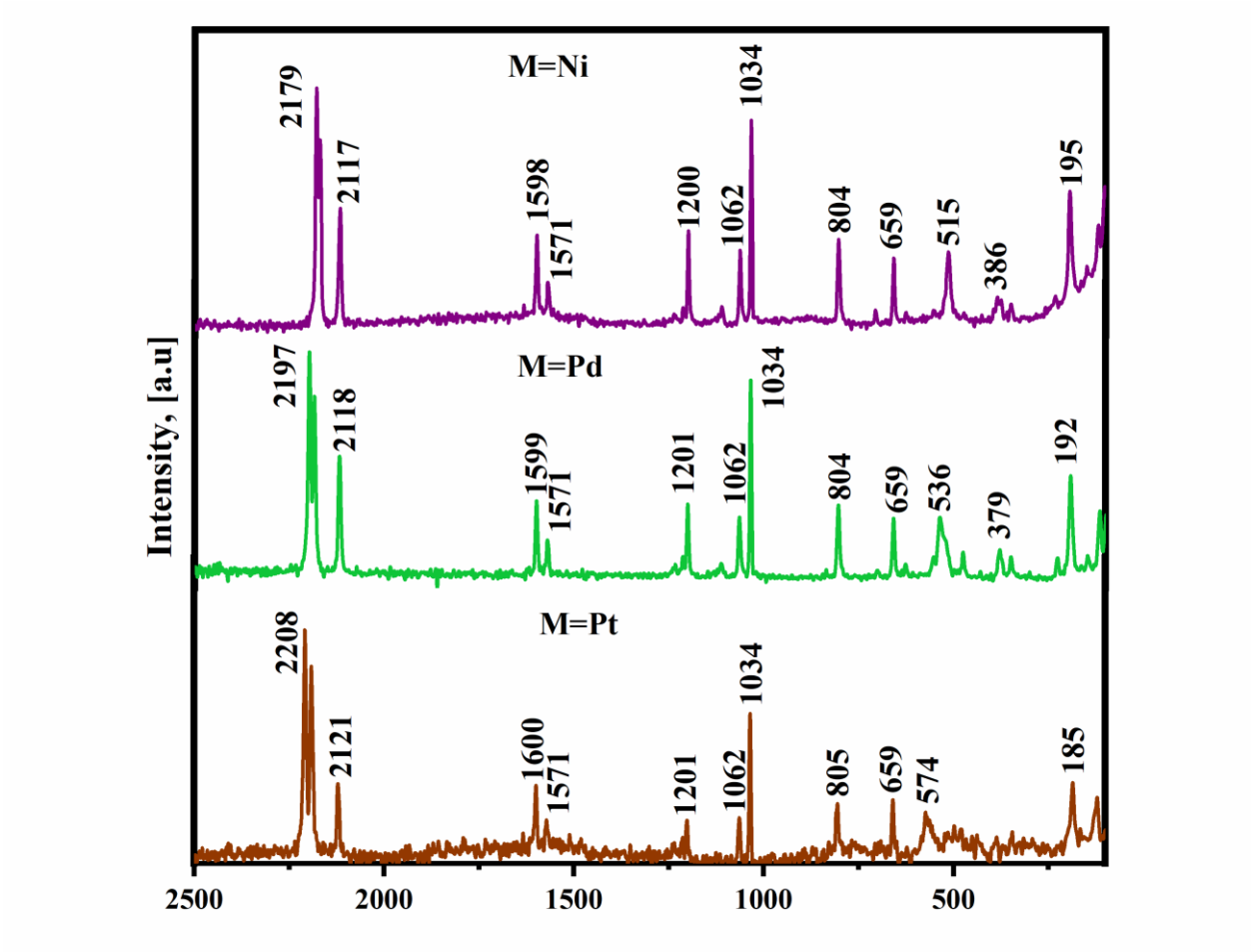

Figure S3: Raman spectra for the Fe(3-Ethynylpyridine)$_2$[M(CN)$_4$] series with M = Ni, Pd, and Pt at 80 K.

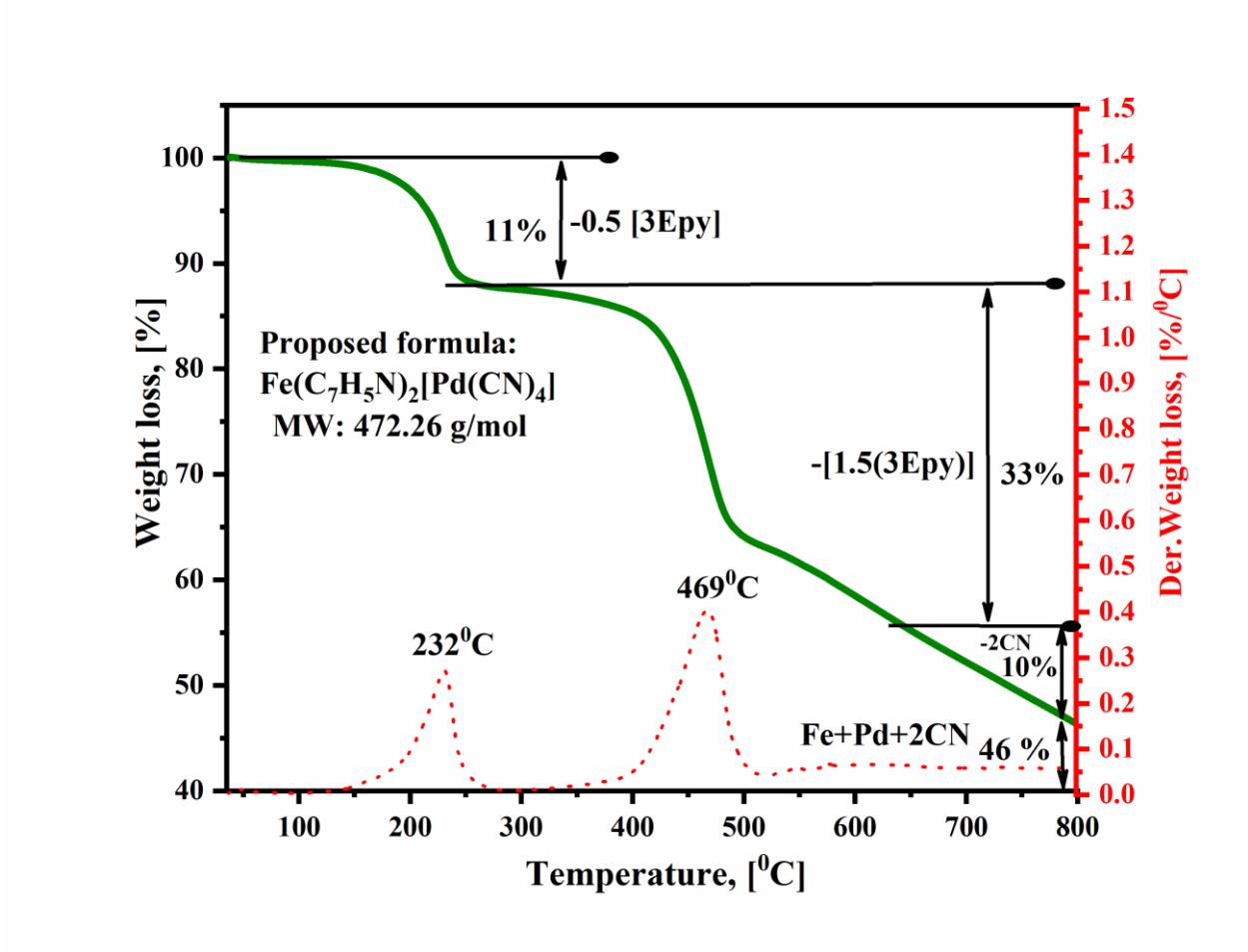

Figure S4: TG curve for the Fe(3-Ethynylpyridine)$_2$[Pd(CN)$_4$].

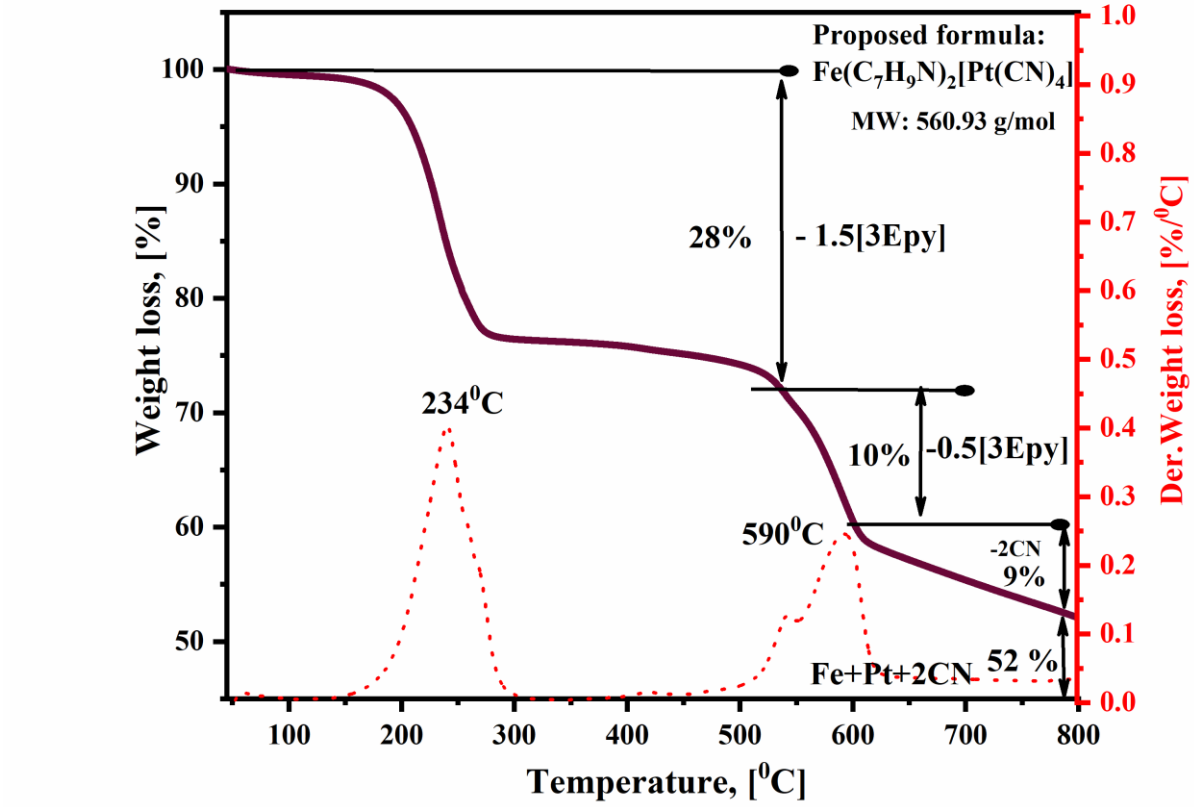

Figure S5: TG curve for the Fe(3-Ethynylpyridine)$_2$[Pt(CN)$_4$].

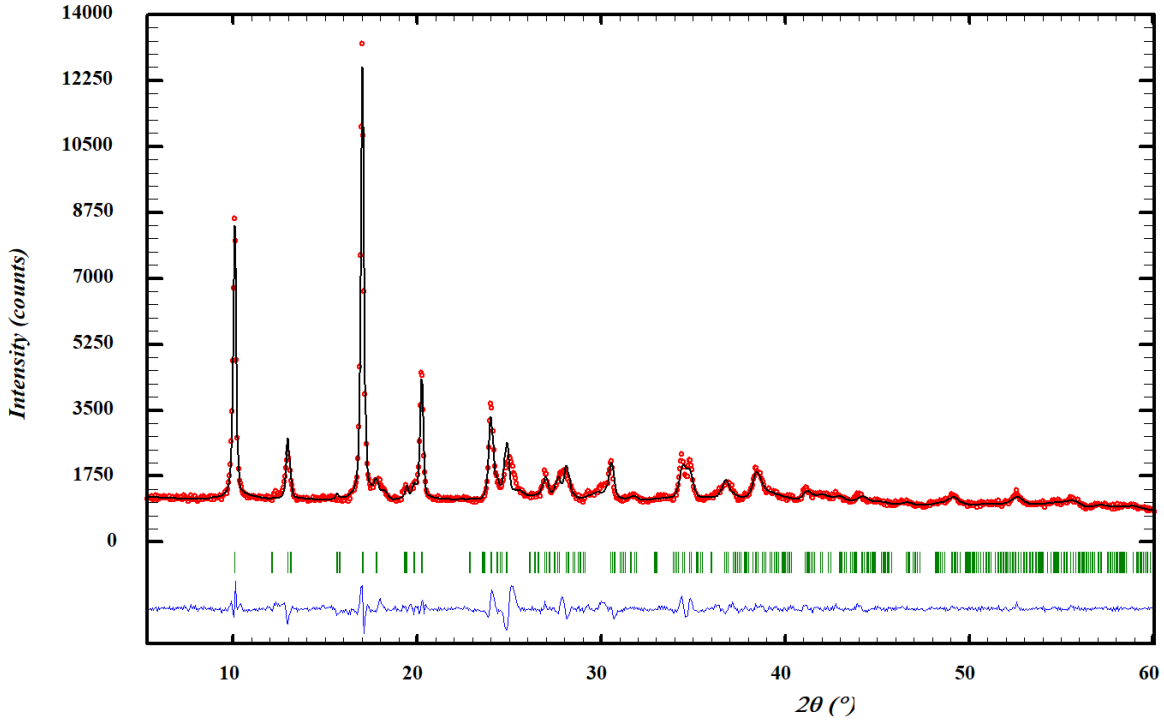

Figure S6. XRD powder pattern experimental (red), calculated (black), and profile fitting difference (blue) for the complex Fe(3-Ethynylpyridine)$_2$[Pt(CN)$_4$]. The experimental pattern was fitted by the Le Bail method. Some spurious reflections are observed.

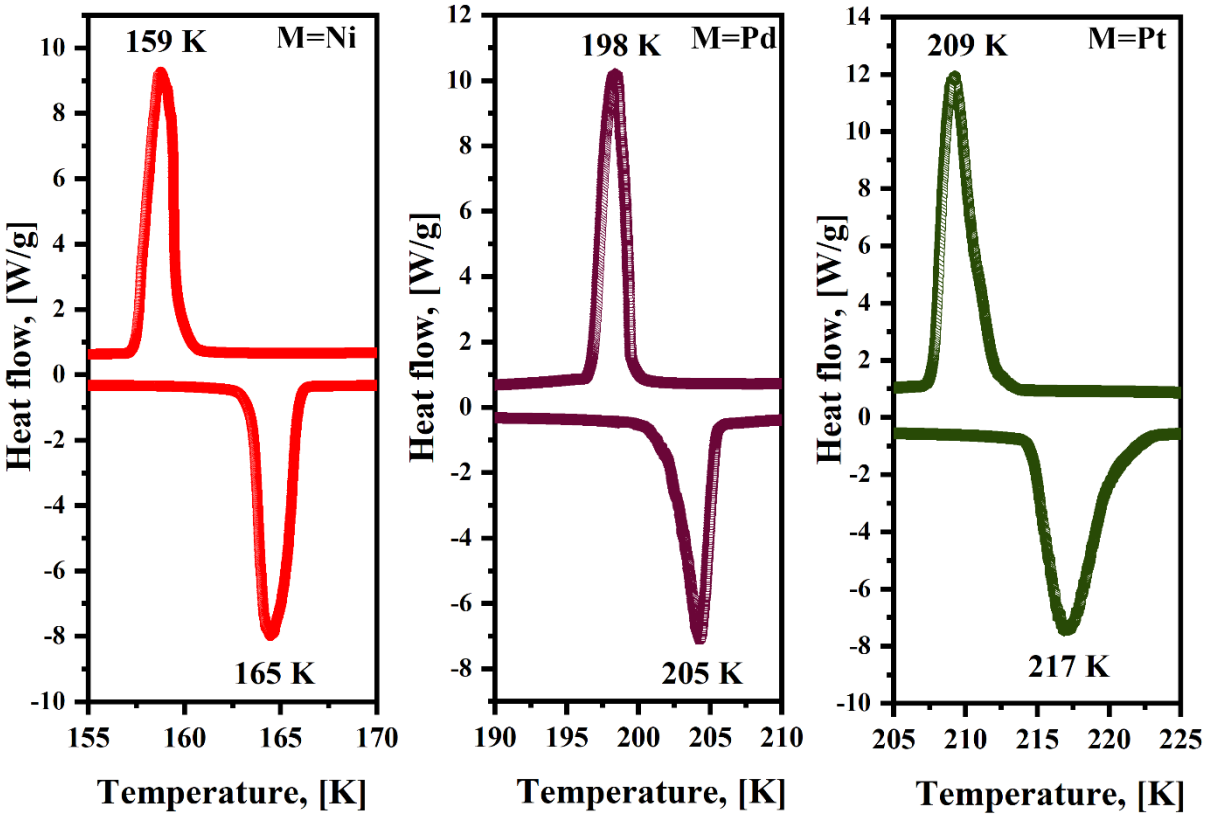

Figure S7. DSC curve for the Fe(3-Ethynylpyridine)$_2$[M(CN)$_4$] series with M = Ni, Pd, and Pt in the temperature region where the spin transitions are observed.

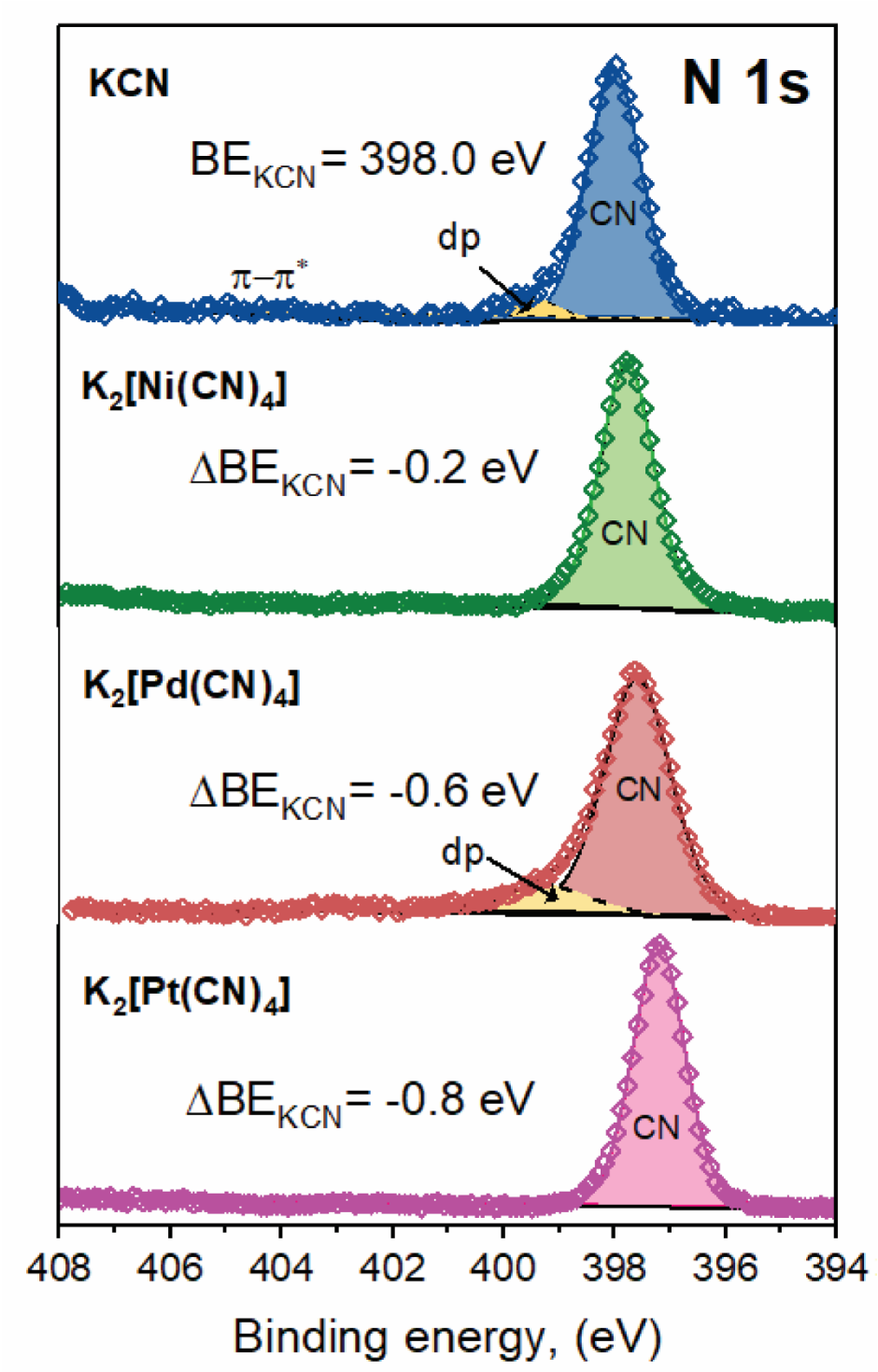

Figure S8. N1s core-level region of the HRXPS spectra for the $K_2[M(CN)_4]$ series, where M = Ni, Pd, Pt. The N1s peak corresponding to KCN, which is free of π-back bonding, was included as a reference. The weak peak labeled as dp was ascribed to decomposition product under the sample irradiation with X-ray under a high vacuum.

Table S1: Details of data collection, crystal data, and structure refinement for Fe(3-Ethynylpyridine)$_2$[M(CN)$_4$] series with M = Ni, and Pd at 300 K.

Temperature	Fe(3-Ethynylpyridine)$_2$[Ni(CN)$_4$]	Fe(3-Ethynylpyridine)$_2$[Pd(CN)$_4$]
Wavelength (Å)	1.5418	
2θ range (°)	6-60	
Step size (°)	0.01	
Time per step (s)	0.01	
Crystal system	*Orthorhombic*	
Space Group	*$P2_1\ 2_12$*	*$P2_1\ 2_12$*
Parameter (Å)	17.604 (5)	17.639 (1)
	7.008 (3)	7.299 (6)
	7.319 (1)	7.468 (10)
V(Å^3)	902.92 (5)	961.41 (16)
Z	2	2
Refinement		
# of reflections	106	61
# of refined parameters		
Structural	52	52
Profile	11	11
R_{exp}	2.74	2.46
R_{wp}	4.61	3.40
R_B	5.52	4.80
S	1.68	1.38

Table S2: Unit cell parameters for the HS and LS phases reported for Hofmann-like 2D coordination polymers.

Metal	Ligand	**a**, in Å	**b**, in Å	**c**, in Å	V, in Å^3	Volume contraction, %	Ref.
Ni:HS	3-	16.7053(11)	7.1336(4)	7.3280(3)	818.72(8)	6.8	23
LS	chloropyrazine	16.511(2)	6.9222(10)	7.2033(7)	763.07(17)		
Pd:HS	3-	15.657(2)	7.520(1)	7.2930(5)	845.25(17)	8.6	20
LS	fluoropyridine	15.179(4)	7.240(2)	7.0840(15)	772.66(40)		
Pt:HS	3-	15.6840(14)	7.5060(8)	7.2880(9)	843.71(16)	8.6	20
LS	fluoropyridine	15.220(2)	7.2230(13)	7.0770(14)	771.01(20)		
Pd:HS	Phthalazine	7.2433(4)	7.4455(4)	10.4263(9)	497.11(6)	5.7	25
LS		7.0962(7)	7.1676(7)	10.1546(16)	468.49(10)		
Pt:HS	Phthalazine	7.2754(8)	7.4315(9)	10.3903(14)	501.04(11)	5.5	25
LS		7.1262(5)	7.1724(5)	10.1727(8)	473.38(6)		
Ni:HS	Pyridazine	7.222(3)	15.172(7)	7.433(3)	814.45(60)	11.2	24
LS		6.9234(15)	14.676(3)	7.1195(15)	723.4(3)		

Pd:HS LS	Pyridazine	7.365(9) 7.0729(13)	14.969(18) 14.583(3)	7.538(9) 7.2986(13)	831.04(170) 752.81(20)	9.4	24
Pt:HS LS	Pyridazine	7.401(2) 7.0858(9)	15.058(5) 14.587(18)	7.538(2) 7.2887(9)	840.07(50) 753.41(16)	10.3	24
Pt:HS LS	2,4 Bipyridine	7.5176(8) 7.2122(3)	23.803(2) 23.3642(9)	7.3695(7) 7.1140(3)	1318.71(20) 1198.76(8)	9.09	26

Table S3: Chemical analysis results for the obtained polycrystalline materials

Sample	**%Fe**		**%M**		**%C**		**%N**		**%H**	
	Cal.	**Exp.**	**Cal.**	**Exp.**	**Cal.**	**Exp.**	**Cal.**	**Exp.**	**Cal.**	**Exp.**
Ni	13.15	12.89	13.81	13.56	50.85	51.04	19.77	20.05	2.42	2.35
Pd	11.82	11.98	22.53	22.04	45.74	45.99	17.79	17.12	2.12	2.22
Pt	9.95	10.01	34.78	35.07	38.51	37.87	14.97	15.10	1.79	1.56

Table S4. Microstructural analysis for Fe(3-Ethynylpyridine)$_2$[M(CN)$_4$] series with M = Ni, and Pd at 300 K.

Sample	**Average crystallite size (nm)**	**Average maximum strain (a.u.)**
Ni	86.52 (14.98)*	37.67 (7.76)*
Pd	80.11 (23.31)*	72.51 (18.87)*

*) The quantities between parentheses are a measure of the degree of anisotropy, not of the estimated error.

Table S5. Refined atomic positions and thermal (B_{iso}) and occupation (Occ) factors for Fe(3-Ethynylpyridine)$_2$[M(CN)$_4$] series with M = Ni, and Pd at 300 K

Composition	site	x	y	z	Biso	Occ
Fe(3-Ethynylpyridine)$_2$[Ni(CN)$_4$]						
Fe	2b	0	1/2	0.244(3)	3.05(2)	1/2
Ni	2a	0	0	0.774(3)	2.53(2)	1/2
N1	4c	0.024(5)	0.279 (3)	0.472(6)	3.49(1)	1
N2	4c	0.017(5)	0.298(3)	1.067(5)	3.49(1)	1
N3	4c	0.124(7)	0.581(13)	0.254(8)	3.77(1)	1
C1	4c	0.021(7)	0.185(3)	0.599(7)	3.49(1)	1
C2	4c	0.015(7)	0.198(3)	0.942(8)	3.49(1)	1
C3	4c	0.182(5)	0.448(3)	0.251(6)	4.44(1)	1
C4	4c	0.256(6)	0.509(3)	0.247(8)	4.44(1)	1
C5	4c	0.272(5)	0.703(3)	0.246(6)	4.44(1)	1
C6	4c	0.214(5)	0.836(4)	0.248(4)	4.44(1)	1

C7	4c	0.140(4)	0.775(3)	0.253(3)	4.44(1)	1
C8	4c	0.317(4)	0.374(3)	0.244(3)	4.44(1)	1
C9	4c	0.368(3)	0.259(2)	0.241(3)	4.44(1)	1
H1	4c	0.168	0.320	0.253	4.44	1
H2	4c	0.321	0.741	0.241	4.44	1
H3	4c	0.228	0.963	0.247	4.44	1
H4	4c	0.100	0.860	0.255	4.44	1
H5	4c	0.407	0.173	0.239	4.44	1

Composition	site	x	y	z	Biso	Occ
$Fe(3\text{-Ethynylpyridine})_2[Pd(CN)_4]$						
Fe	2b	0	1/2	0.243(4)	2.79(3)	1/2
Pd	2a	0	0	0.762(2)	3.08(3)	1/2
N1	4c	0.011(7)	0.305(5)	0.469(7)	4.59(1)	1
N2	4c	0.013(7)	0.289(5)	1.067(3)	4.59(1)	1
N3	4c	0.120(4)	0.579(8)	0.220(6)	3.94(1)	1
C1	4c	0.009(5)	0.200(5)	0.583(4)	4.59(1)	1
C2	4c	0.009(4)	0.197(5)	0.944(5)	4.59(1)	1
C3	4c	0.167(3)	0.428(5)	0.243(4)	4.19(4)	1
C4	4c	0.244(6)	0.452(1)	0.254(6)	4.19(2)	1
C5	4c	0.275(3)	0.626(5)	0.242(7)	4.19(3)	1
C6	4c	0.229(7)	0.777(2)	0.219(2)	4.19(1)	1
C7	4c	0.151(5)	0.754(1)	0.208(4)	4.19(2)	1
C8	4c	0.293(3)	0.297(4)	0.278(6)	4.19(1)	1
C9	4c	0.334(4)	0.166(3)	0.298(4)	4.19(4)	1
H1	4c	0.143	0.316	0.252	4.19	1
H2	4c	0.326	0.643	0.251	4.19	1
H3	4c	0.251	0.891	0.210	4.19	1
H4	4c	0.119	0.850	0.190	4.19	1
H5	4c	0.366	0.064	0.316	4.19	1

Table S6. Calculated inter-atomic distances (in Å) and bond angles (in °) from the refined crystal structure for $Fe(3\text{-Ethynylpyridine})_2[M(CN)_4]$ series with M = Ni, and Pd at 300 K

Bond distance (Å)	Angles (°)
$Fe(3\text{-Ethynylpyridine})_2[Ni(CN)_4]$ at 300 K	

Fe-N1 = 2.32(3)	N1-Fe-N2 = 87.99(1)	N3-C7-C6 = 119.59(1)
Fe-N2 = 1.94(3)	N2-Fe-N1 = 174.92(1)	C4-C8-C9 = 179.94(1)
Fe-N3 = 2.25(3)	N3-Fe-N3 = 176.11(1)	N3-C3-H1 = 117.00
Ni-C1 = 1.86(3)	N1-Fe-N1 = 87.70(1)	C4-C3-H1 = 124.00
Ni-C2 = 1.87(3)	N2-Fe-N2 = 96.43(1)	C4-C5-H2 = 120.00
C1-N1 = 1.14(2)	N1-Fe-N3 = 87.47(1)	C6-C5-H2 = 120.00
C2-N2 = 1.15(2)	N1-Fe-N3 = 89.73(1)	C5-C6-H3 = 118.00
N3-C3 = 1.38(2)	N3-Fe-N2 = 89.83(1)	C7-C6-H3 = 123.00
C3-C4 = 1.38(2)	N3-Fe-N2 = 92.76(1)	N3-C7-H4 = 120.00
C4-C5 = 1.38(2)	C1-Ni-C2 = 175.15(1)	C6-C7-H4 = 120.00
C5-C6 = 1.38(2)	C1-Ni-C1 = 93.13(1)	C8-C9-H5 = 180.00
C6-C7 = 1.38(2)	C2-Ni-C1 = 84.51(1)	
C4-C8 = 1.43(2)	C2-Ni-C2 = 98.15(1)	
C8-C9 = 1.21(2)	N1-C1-Ni = 166.49(1)	
	N2-C2-Ni = 167.16(1)	
	C1-N1-Fe = 164.79(1)	
	C2-N2-Fe = 165.11(1)	
	C3-N3-C7 = 120.87(1)	
	C3-N3-Fe = 123.64(1)	
	Fe-N3-C7 = 115.39(1)	
	N3-C3-C4 = 119.49(1)	
	C3-C4-C5 = 119.68(1)	
	C3-C4-C8 = 120.26(1)	
	C5-C4-C8 = 120.06(1)	
	C4-C5-C6 = 120.84(1)	
	C5-C6-C7 = 119.54(1)	

Bond distance (Å)	Angles (°)	
$Fe(3\text{-Ethynylpyridine})_2[Pd(CN)_4]$ at 300 K		
Fe-N1 = 2.22(3)	N1-Fe-N2 = 90.00(1)	N3-C7-C6 = 119.59(1)
Fe-N2 = 2.04(3)	N2-Fe-N1 = 170.74(1)	C4-C8-C9 = 179.93(1)
Fe-N3 = 2.21(3)	N3-Fe-N3 = 170.86(1)	N3-C3-H1 = 117.00
Pd-C1 = 1.99(3)	N1-Fe-N1 = 80.75(1)	C4-C3-H1 = 124.00
Pd-C2 = 1.99(3)	N2-Fe-N2 = 99.26(1)	C4-C5-H2 = 120.00
C1-N1 = 1.14(3)	N1-Fe-N3 = 88.55(1)	C6-C5-H2 = 120.00
C2-N2 = 1.14(3)	N1-Fe-N3 = 98.44(1)	C5-C6-H3 = 120.00
N3-C3 = 1.38(3)	N3-Fe-N2 = 81.68(1)	C7-C6-H3 = 122.00
C3-C4 = 1.38(3)	N3-Fe-N2 = 92.38(1)	N3-C7-H4 = 120.00
C4-C5 = 1.38(3)	C1-Pd-C2 = 179.10(1)	C6-C7-H4 = 120.00
C5-C6 = 1.38(3)	C1-Pd-C1 = 95.34(1)	C8-C9-H5 = 180.00
C6-C7 = 1.38(3)	C2-Pd-C1 = 85.52(1)	
C4-C8 = 1.43(3)	C2-Pd-C2 = 93.63(1)	
C8-C9 = 1.21(3)	N1-C1-Pd = 174.63(1)	
	N2-C2-Pd = 169.62(1)	
	C1-N1-Fe = 172.98(1)	
	C2-N2-Fe = 164.07(1)	
	C3-N3-C7 = 120.87(1)	

	C3-N3-Fe = 110.38(1) Fe-N3-C7 = 128.23(1) N3-C3-C4 = 119.48(1) C3-C4-C5 = 119.68(1) C3-C4-C8 = 120.26(1) C5-C4-C8 = 120.07(1) C4-C5-C6 = 120.84(1) C5-C6-C7 = 119.54(1)

Table S7. Calculated atomic positions for HS phase of Fe(3-Ethynylpyridine)$_2$[Pt(CN)$_4$].

Composition	site	x	y	z	Biso	Occ
Fe(3-Ethynylpyridine)$_2$[Pt(CN)$_4$]						
Pt	2a	0	0	0.764(7)	3.08(2)	1/2
Fe	2b	0	0.5	0.246(6)	2.79(2)	1/2
N1	4c	0.011(6)	0.309(5)	0.471(6)	4.59(1)	1
N2	4c	0.014(3)	0.304(7)	1.067(6)	4.59(1)	1
N3	4c	0.121(7)	0.577(8)	0.229(5)	3.94(1)	1
C1	4c	0.008(2)	0.196(3)	0.583(5)	4.59(1)	1
C2	4c	0.011(3)	0.189(4)	0.957(2)	4.59(1)	1
C3	4c	0.169(3)	0.434(5)	0.247(7)	4.19(1)	1
C4	4c	0.249(6)	0.450(3)	0.251(8)	4.19(1)	1
C5	4c	0.279(5)	0.626(3)	0.242(6)	4.19(1)	1
C6	4c	0.231(5)	0.772(4)	0.217(4)	4.19(1)	1
C7	4c	0.153(2)	0.748(1)	0.216(4)	4.19(1)	1
C8	4c	0.296(1)	0.297(3)	0.283(1)	4.19(1)	1
C9	4c	0.339(3)	0.167(2)	0.301(3)	4.19(1)	1
H1	4c	0.142	0.301	0.257	4.19	1
H2	4c	0.341	0.642	0.250	4.19	1
H3	4c	0.256	0.910	0.202	4.19	1
H4	4c	0.114	0.863	0.193	4.19	1
H5	4c	0.378	0.056	0.325	4.19	1

Table S8. Inter-atomic distances (in Å) and bond angles (in °) from the calculated crystal structure for the HS phase of Fe(3-Ethynylpyridine)$_2$[Pt(CN)$_4$].

Bond distance (Å)	Angles (°)	
Fe(3-Ethynylpyridine)$_2$[Pt(CN)$_4$]		
Fe-N1 = 2.19(3)	N1-Fe-N2 = 92.12(8)	N3-C7-C6 = 121.13(2)
Fe-N2 = 1.97(2)	N2- Fe-N1 = 172.42(1)	C4-C8-C9 = 176.25(1)
Fe-N3 = 2.21(3)	N3- Fe-N3 = 173.28(1)	N3-C3-H1 = 117.00
Pt-C1 = 1.98(2)	N1- Fe-N1 = 80.46(8)	C4-C3-H1 = 120.00
Pt-C2 = 2.00(2)	N2- Fe-N2 = 95.33(8)	C4-C5-H2 = 118.00

C1-N1 = 1.17(14)	N1-Fe-N3 = 88.03(2)	C6-C5-H2 = 122.00
C2-N2 = 1.17(14)	N1-Fe-N3 = 97.12(2)	C5-C6-H3 = 120.00
N3-C3 = 1.35(1)	N3-Fe-N2 = 84.10(2)	C7-C6-H3 = 122.00
C3-C4 = 1.41(1)	N3-Fe-N2 = 91.36(3)	N3-C7-H4 = 118.00
C4-C5 = 1.40(1)	C1-Pt-C2 = 176.74(1)	C6-C7-H4 = 120.00
C5-C6 = 1.37(1)	C1-Pt-C1 = 94.08(8)	C8-C9-H5 = 176.00
C6-C7 = 1.39(2)	C2-Pt-C1 = 88.65(8)	
C4-C8 = 1.42(4)	C2-Pt-C2 = 88.68(8)	
C8-C9 = 1.22(2)	N1-C1-Pt = 177.68(1)	
	N2-C2-Pt = 173.17(4)	
	C1-N1-Fe = 166.03(4)	
	C2-N2-Fe = 176.95(1)	
	C3-N3-C7 = 117.72(6)	
	C3-N3-Fe = 113.29(5)	
	Fe-N3-C7 = 128.80(1)	
	N3-C3-C4 = 123.96(4)	
	C3-C4-C5 = 119.68(1)	
	C3-C4-C8 = 116.93(2)	
	C5-C4-C8 = 121.00(6)	
	C4-C5-C6 = 119.79(6)	
	C5-C6-C7 = 120.27(4)	

Table S9. Calculated atomic positions for the phase of low temperature for Fe(3-Ethynylpyridine)$_2$[M(CN)$_4$] series with M = Ni, Pd, and Pt.

Composition	site	x	y	z	Biso	Occ
Fe(3-Ethynylpyridine)$_2$[Ni(CN)$_4$]						
Ni	2a	0	0	0.765(5)	3.05(2)	½
Fe	2b	0	0.5	0.263(3)	2.53(2)	1/2
N1	4c	0.021(5)	0.304(3)	0.464(6)	3.49(1)	1
N2	4c	0.014(5)	0.306(3)	1.070(5)	3.49(1)	1
N3	4c	0.113(7)	0.574(13)	0.252(8)	3.77(1)	1
C1	4c	0.021(7)	0.182(3)	0.580(7)	3.49(1)	1
C2	4c	0.014(7)	0.192(3)	0.948(8)	3.49(1)	1
C3	4c	0.171(5)	0.443(3)	0.250(6)	4.44(1)	1
C4	4c	0.249(6)	0.499(3)	0.250(8)	4.44(1)	1
C5	4c	0.266(5)	0.699(3)	0.250(6)	4.44(1)	1
C6	4c	0.207(5)	0.836(4)	0.249(4)	4.44(1)	1
C7	4c	0.130(4)	0.768(3)	0.251(3)	4.44(1)	1
C8	4c	0.309(4)	0.357(5)	0.249(3)	4.44(1)	1
C9	4c	0.364(3)	0.247(2)	0.236(3)	4.44(1)	1
H1	4c	0.154	0.290	0.250	4.44	1
H2	4c	0.327	0.746	0.250	4.44	1
H3	4c	0.219	0.994	0.250	4.44	1

H4	4c	0.082	0.870	0.262	4.44	1
H5	4c	0.407	0.133	0.240	4.44	1

Composition	site	x	y	z	Biso	Occ
$Fe(3\text{-Ethynylpyridine})_2[Pd(CN)_4]$						
Pd	2a	0	0	0.758(5)	3.08(3)	1/2
Fe	2b	0	0.5	0.248(3)	2.79(3)	1/2
N1	4c	0.014(5)	0.304(3)	0.446(6)	4.59(1)	1
N2	4c	0.014(5)	0.305(3)	1.068(5)	4.59(1)	1
N3	4c	0.113(7)	0.576(2)	0.231(8)	3.94(1)	1
C1	4c	0.007(7)	0.197(3)	0.567(7)	4.59(1)	1
C2	4c	0.007(7)	0.197(3)	0.949(8)	4.59(1)	1
C3	4c	0.162(5)	0.428(3)	0.237(6)	4.19(4)	1
C4	4c	0.243(6)	0.447(3)	0.250(8)	4.19(2)	1
C5	4c	0.276(5)	0.627(3)	0.236(6)	4.19(3)	1
C6	4c	0.227(5)	0.776(4)	0.216(4)	4.19(1)	1
C7	4c	0.146(4)	0.746(3)	0.216(3)	4.19(2)	1
C8	4c	0.291(4)	0.293(3)	0.281(3)	4.19(1)	1
C9	4c	0.334(3)	0.160(2)	0.302(3)	4.19(4)	1
H1	4c	0.136	0.289	0.25	4.19	1
H2	4c	0.339	0.645	0.248	4.19	1
H3	4c	0.251	0.916	0.206	4.19	1
H4	4c	0.106	0.86	0.196	4.19	1
H5	4c	0.374	0.047	0.326	4.19	1

Composition	site	x	y	z	Biso	Occ
$Fe(3\text{-Ethynylpyridine})_2[Pt(CN)_4]$						
Pt	2a	0	0	0.761(7)	3.08(2)	1/2
Fe	2b	0	0.5	0.253(6)	2.79(2)	1/2
N1	4c	0.014(6)	0.314(5)	0.450(6)	4.59(1)	1
N2	4c	0.015(3)	0.314(7)	1.064(6)	4.59(1)	1
N3	4c	0.113(7)	0.568(8)	0.234(5)	3.94(1)	1
C1	4c	0.009(2)	0.200(3)	0.566(5)	4.59(1)	1
C2	4c	0.009(3)	0.199(4)	0.951(2)	4.59(1)	1
C3	4c	0.16101(3)	0.42526(5)	0.250(7)	4.19(1)	1
C4	4c	0.24301(6)	0.44526(3)	0.250(8)	4.19(1)	1
C5	4c	0.27401(5)	0.62526(3)	0.236(6)	4.19(1)	1
C6	4c	0.22401(5)	0.77426(4)	0.217(4)	4.19(1)	1
C7	4c	0.14301(4)	0.74226(3)	0.217(3)	4.19(1)	1
C8	4c	0.28901(4)	0.29126(3)	0.281(3)	4.19(1)	1
C9	4c	0.33201(3)	0.15826(2)	0.302(3)	4.19(1)	1
H1	4c	0.137	0.285	0.261	4.19	1
H2	4c	0.337	0.642	0.246	4.19	1
H3	4c	0.248	0.913	0.208	4.19	1

H4	4c	0.103	0.860	0.193	4.19	1
H5	4c	0.372	0.048	0.326	4.19	1

Table S10. Interatomic distances (in Å) and bond angles (in °) from the calculated crystal structure for the phase of low temperature for Fe(3-Ethynylpyridine)$_2$[M(CN)$_4$] series with M = Ni, Pd, and Pt.

Bond distance (Å)	Angles (°)	
Fe(3-Ethynylpyridine)$_2$[Ni(CN)$_4$]		
Fe-N1 = 1.99(1)	N1-Fe-N2 = 89.74(1)	N3-C7-C6 = 122.14(1)
Fe-N2 = 1.92(1)	N2-Fe-N1 = 177.39(1)	C4-C8-C9 = 173.47(1)
Fe-N3 = 2.01(1)	N3-Fe-N3 = 176.11(1)	N3-C3-H1 = 117.00
Ni-C1 = 1.85(1)	N1-Fe-N1 = 91.52(1)	C4-C3-H1 = 120.00
Ni-C2 = 1.86(1)	N2-Fe-N2 = 89.10(1)	C4-C5-H2 = 120.00
C1-N1 = 1.17(7)	N1-Fe-N3 = 91.55(1)	C6-C5-H2 = 122.00
C2-N2 = 1.17(8)	N1-Fe-N3 = 90.97(1)	C5-C6-H3 = 120.00
N3-C3 = 1.35(8)	N3-Fe-N2 = 91.29(1)	C7-C6-H3 = 119.00
C3-C4 = 1.39(8)	N3-Fe-N2 = 86.14(1)	N3-C7-H4 = 116.00
C4-C5 = 1.39(8)	C1-Ni-C2 = 175.15(1)	C6-C7-H4 = 120.00
C5-C6 = 1.37(8)	C1-Ni-C1 = 87.53(1)	C8-C9-H5 = 173.00
C6-C7 = 1.39(8)	C2-Ni-C1 = 90.20(3)	
C4-C8 = 1.41(8)	C2-Ni-C2 = 92.26(1)	
C8-C9 = 1.22(8)	N1-C1-Ni = 170.40(1)	
	N2-C2-Ni = 172.26(1)	
	C1-N1-Fe = 168.51(1)	
	C2-N2-Fe = 171.80(1)	
	C3-N3-C7 = 124.83(1)	
	C3-N3-Fe = 124.83(1)	
	Fe-N3-C7 = 118.52(1)	
	N3-C3-C4 = 123.89(1)	
	C3-C4-C5 = 118.25(1)	
	C3-C4-C8 = 120.17(1)	
	C5-C4-C8 = 121.58(1)	
	C4-C5-C6 = 118.85(1)	
	C5-C6-C7 = 120.23(1)	

Bond distance (Å)	Angles (°)	
Fe(3-Ethynylpyridine)$_2$[Pd(CN)$_4$]		
Fe-N1 = 2.02(2)	N1-Fe-N2 = 90.98(6)	N3-C7-C6 = 121.71(1)
Fe-N2 = 1.93(2)	N2-Fe-N1 = 178.03(1)	C4-C8-C9 = 177.61(1)
Fe-N3 = 2.01(2)	N3-Fe-N3 = 172.69(1)	N3-C3-H1 = 117.00
Pd-C1 = 1.98(2)	N1-Fe-N1 = 87.05(6)	C4-C3-H1 = 120.00
Pd-C2 = 1.98(2)	N2-Fe-N2 = 90.99(6)	C4-C5-H2 = 120.00
C1-N1 = 1.17(2)	N1-Fe-N3 = 88.65(2)	C6-C5-H2 = 122.00
C2-N2 = 1.16(2)	N1-Fe-N3 = 96.66(2)	C5-C6-H3 = 120.00

N3-C3 = 1.35(1)	N3-Fe-N2 = 83.32(2)	C7-C6-H3 = 122.00
C3-C4 = 1.37(1)	N3-Fe-N2 = 91.54(2)	N3-C7-H4 = 116.00
C4-C5 = 1.41(1)	C1-Pd-C2 = 179.06(1)	C6-C7-H4 = 122.00
C5-C6 = 1.38(1)	C1-Pd-C1 = 92.98(6)	C8-C9-H5 = 175.00
C6-C7 = 1.41(1)	C2-Pd-C1 = 87.95(6)	
C4-C8 = 1.40(3)	C2-Pd-C2 = 91.12(6)	
C8-C9 = 1.21(2)	N1-C1-Pd = 177.69(1)	
	N2-C2-Pd = 178.84(1)	
	C1-N1-Fe = 168.03(1)	
	C2-N2-Fe = 167.80(1)	
	C3-N3-C7 = 119.26(5)	
	C3-N3-Fe = 111.98(4)	
	Fe-N3-C7 = 128.76(1)	
	N3-C3-C4 = 121.84(3)	
	C3-C4-C5 = 119.27(1)	
	C3-C4-C8 = 120.26(1)	
	C5-C4-C8 = 120.07(1)	
	C4-C5-C6 = 118.97(5)	
	C5-C6-C7 = 118.54(4)	

Bond distance (Å)	Angles (°)	
$Fe(3\text{-Ethynylpyridine})_2[Pt(CN)_4]$		
Fe-N1 = 1.96(1)	N1-Fe-N2 = 93.41(4)	N3-C7-C6 = 121.81(1)
Fe-N2 = 1.92(2)	N2-Fe-N1 = 175.94(1)	C4-C8-C9 = 177.14(1)
Fe-N3 = 1.99(3)	N3-Fe-N3 = 172.78(1)	N3-C3-H1 = 119.00
Pt-C1 = 2.01(2)	N1-Fe-N1 = 82.53(4)	C4-C3-H1 = 118.00
Pt-C2 = 1.98(2)	N2-Fe-N2 = 90.65(4)	C4-C5-H2 = 118.00
C1-N1 = 1.17(14)	N1-Fe-N3 = 90.21(1)	C6-C5-H2 = 122.00
C2-N2 = 1.16(14)	N1-Fe-N3 = 95.22(1)	C5-C6-H3 = 120.00
N3-C3 = 1.33(1)	N3-Fe-N2 = 84.59(1)	C7-C6-H3 = 122.00
C3-C4 = 1.40(1)	N3-Fe-N2 = 90.33(1)	N3-C7-H4 = 118.00
C4-C5 = 1.40(1)	C1-Pt-C2 = 179.60(1)	C6-C7-H4 = 120.00
C5-C6 = 1.38(1)	C1-Pt-C1 = 92.53(4)	C8-C9-H5 = 176.00
C6-C7 = 1.39(2)	C2-Pt-C1 = 87.86(4)	
C4-C8 = 1.42(4)	C2-Pt-C2 = 91.76(4)	
C8-C9 = 1.21(2)	N1-C1-Pt = 176.53(1)	
	N2-C2-Pt = 178.24(1)	
	C1-N1-Fe = 164.46(1)	
	C2-N2-Fe = 166.54(1)	
	C3-N3-C7 = 118.86(3)	
	C3-N3-Fe = 113.48(3)	
	Fe-N3-C7 = 127.61(1)	
	N3-C3-C4 = 122.55(2)	
	C3-C4-C5 = 118.31(1)	
	C3-C4-C8 = 119.24(2)	
	C5-C4-C8 = 122.20(3)	
	C4-C5-C6 = 119.25(3)	

	C5-C6-C7 = 119.22(3)

Table S11. Solid contraction on the HS → LS spin transition according to the reported structural information for Hofmann-like 2D coordination polymers, $FeL_2[M(CN)_4]$

Metal (M)	Ligand	Fe-L_2-Fe, in Å	Contraction, %	Fe-N≡C-M, in Å	Contraction, %	Reference
Ni: HS	3-	16.705	1.16	5.113	2.31	23
LS	chloropyrazine	16.511		4.995		
Pd: HS	3-	15.657	3.05	5.238	3.30	20
LS	fluoropyridine	15.179		5.065		
Pt: HS	3-	15.684	2.95	5.231	3.34	20
LS	fluoropyridine	15.220		5.056		
Pd: HS	Phthalazine	10.426	2.59	5.196	3.04	25
LS		10.155		5.038		
Pt: HS	Phthalazine	10.390	2.09	5.199	2.80	25
LS		10.173		5.053		
Ni: HS	Pyridazine*	15.172	3.27	5.182	4.19	24
LS		14.676		4.965		
Pd: HS	Pyridazine*	14.969	2.58	5.269	3.54	24
LS		14.583		5.082		
Pt: HS	Pyridazine*	15.058	3.12	5.282	3.77	24
LS		14.588		5.083		
Pt: HS	2,4 Bypiridine	23.803	1.84	5.264	3.95	26
LS		23.364		5.065		

*Fe(Pyridazine)$[M(CN)_4]$•H_2O

Validation of the Computational crystal structure relaxation method, HS → LS

Table S12: Unit cell parameters, experimental and calculated, for Fe(3-Chloropyrazine)$_2[Ni(CN)_4]$.

300 K, experimental **HS phase**	170K, experimental **LS phase**	Calculated **LS phase**
C 1 2/m 1 (12) - monoclinic a[Å]= 16.7053(11) b [Å]= 7.1336(4) c [Å]= 7.3280(3) β=110.358(5)° V [$Å^3$]= 818.72(8) Z=2	C 1 2/m 1 (12) - monoclinic a[Å]= 16.511(2) b [Å]= 6.9222(10) c [Å]= 7.2033(7) β= 112.050(12)° V [$Å^3$]= 763.07(17) Z=2	C 1 2/m 1 (12) - monoclinic a[Å]= 16.4214(4) b [Å]= 7.0900(2) c [Å]= 7.1756(8) β= 112.1664(3)° V [$Å^3$]= 773.7064(76) Z=2

Table S13: Unit cell parameters, experimental and calculated, for Fe(3-Fluoropyridine)$_2$[Pd(CN)$_4$].

300 K, experimental **HS phase**	180K, experimental **LS phase**	Calculated **LS phase**
C 1 2/m 1 (12) - monoclinic a[Å]= 15.657(2) b [Å]= 7.520(1) c [Å]= 7.2930(5) β= 100.148(7)° V [Å^3]= 845.25(17) Z=2	C 1 2/m 1 (12) - monoclinic a[Å]= 15.179(4) b [Å]= 7.240(2) c [Å]= 7.0840(15) β= 97.027(18)° V [Å^3]= 772.66(40) Z=2	C 1 2/m 1 (12) - monoclinic a[Å]= 15.1332(3) b [Å]= 7.1129(2) c [Å]= 7.2448(3) β= 93.6123(14)° V [Å^3]= 778.291(23) Z=2

Table S14: Unit cell parameters, experimental and calculated, for Fe(3-Fluoropyridine)$_2$[Pt(CN)$_4$].

300 K, experimental **HS phase**	180K, experimental **LS phase**	Calculated **LS phase**
C 1 2/m 1 (12) - monoclinic a[Å]= 15.6840(14) b [Å]= 7.5060(8) c [Å]= 7.2880(9) β= 100.462(6)° V [Å^3]= 843.71(16) Z=2	C 1 2/m 1 (12) - monoclinic a[Å]= 15.220(2) b [Å]= 7.2230(13) c [Å]= 7.0770(14) β= 97,688 (10)° V [Å^3]= 771.01(20)) Z=2	C 1 2/m 1 (12) - monoclinic a[Å]= 15.181(6) b [Å]= 7.1811(3) c [Å]= 7.2144(5) β= 99.332 (4)° V [Å^3]= 776.115(9) Z=2