Electronic Supplementary Information

A New Bis(thioether)-Dipyrrin N_2S_2 Ligand and Its Coordination Behaviors to Nickel, Copper and Zinc

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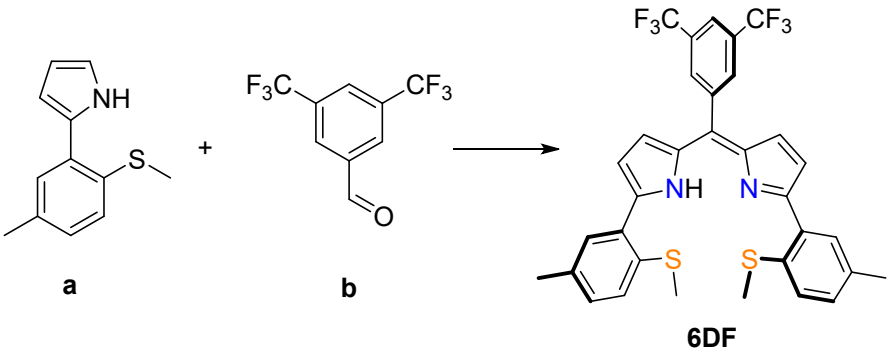


Scheme S1. Synthesis of ligand **6DFH**.

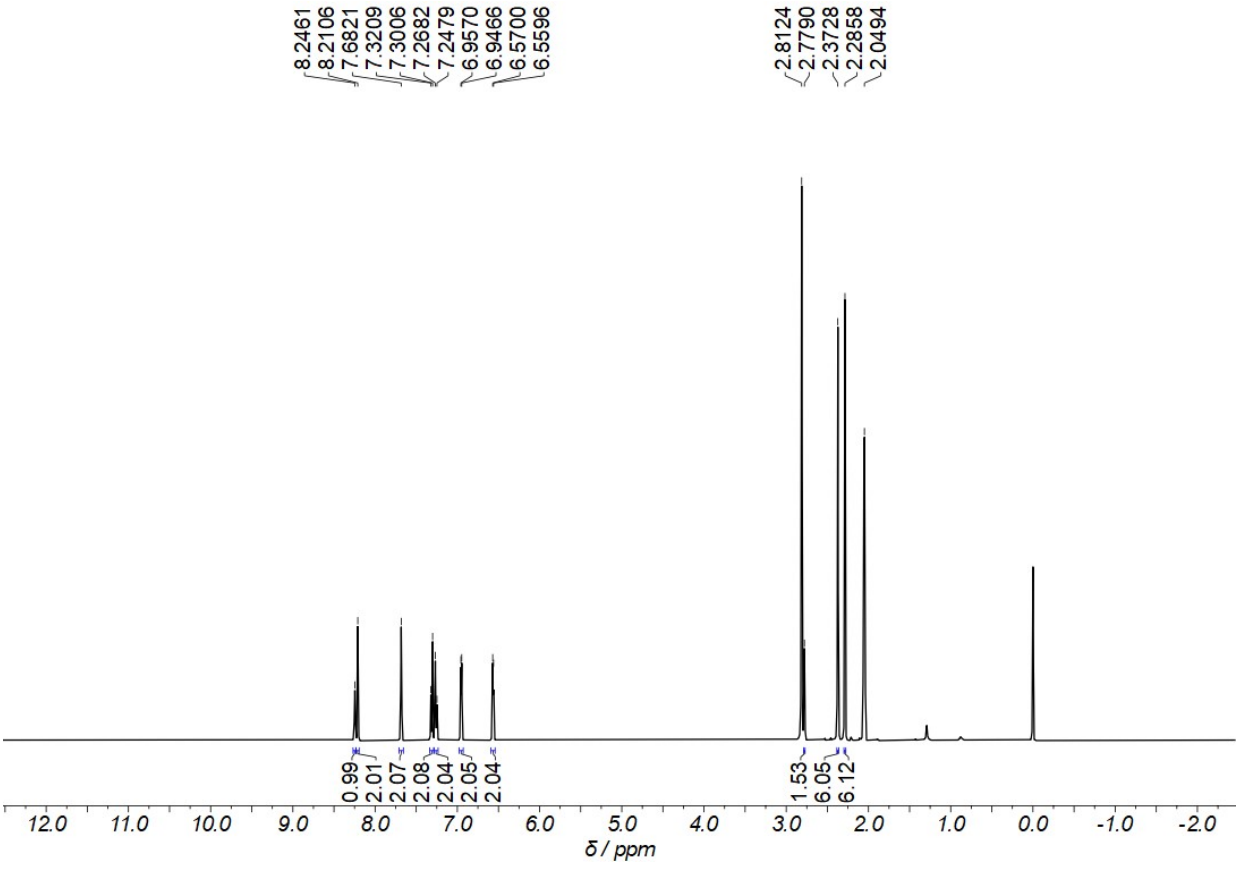


Figure S1. ^{1}H NMR spectrum of ligand **6DFH** in d-acetone at 25 °C.

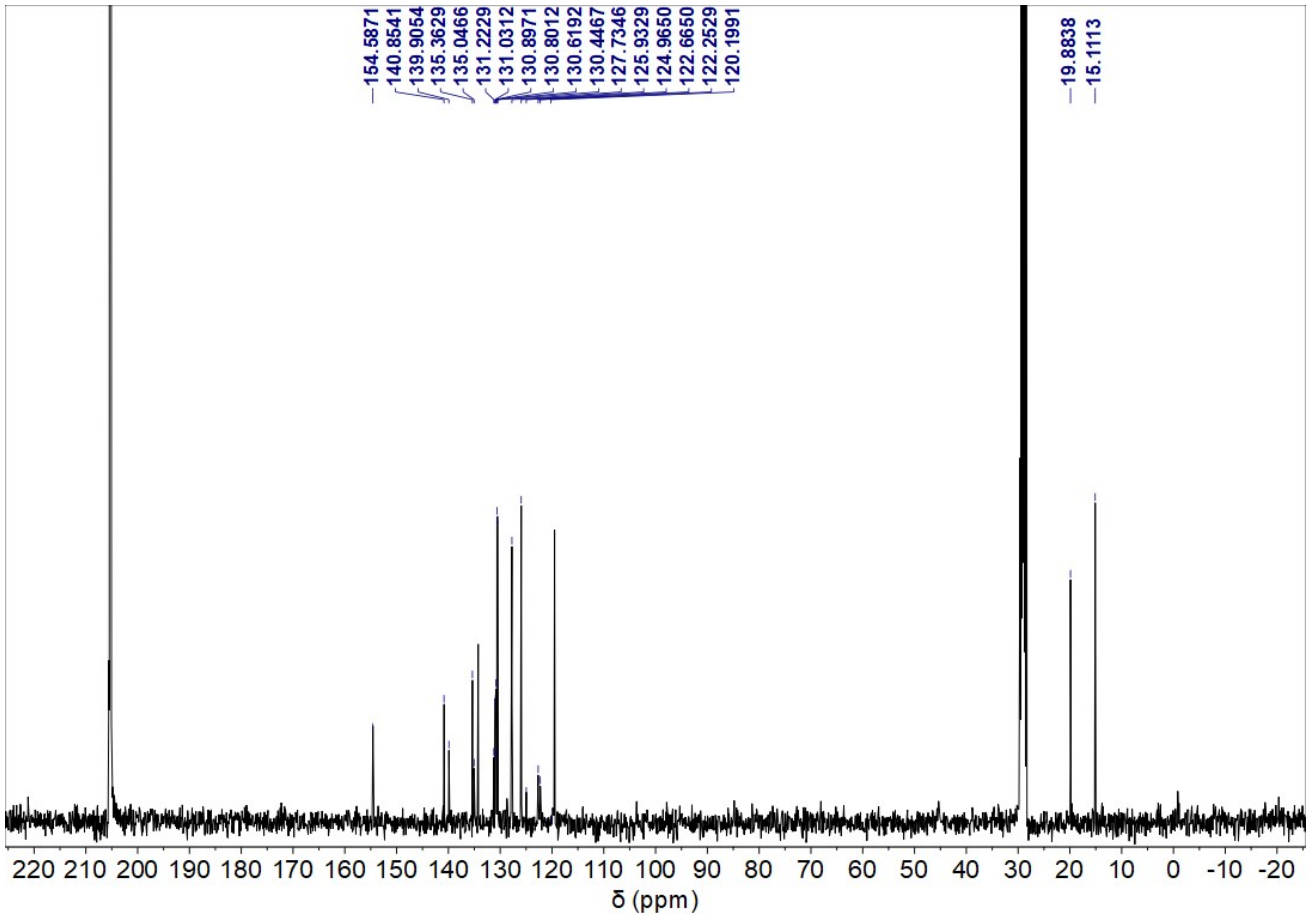


Figure S2. ^{13}C NMR spectrum of ligand **6DFH** in d-acetone at 25 ℃.

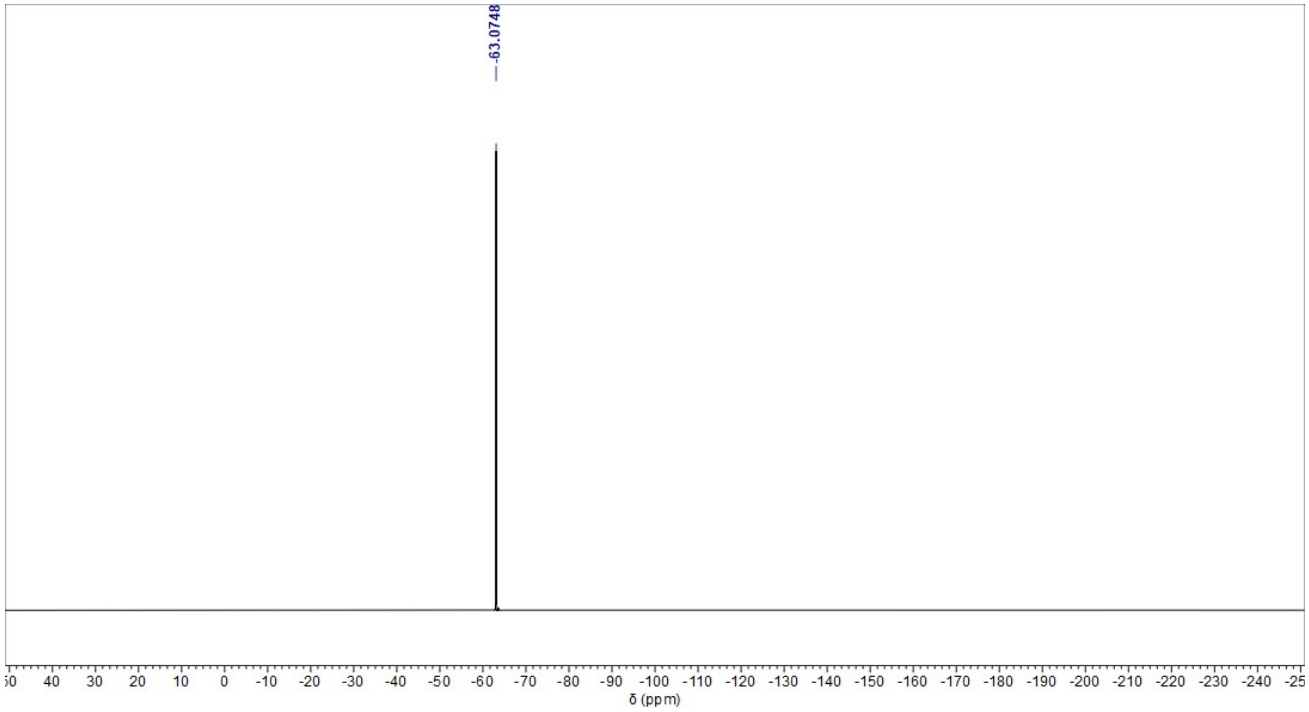


Figure S3. ^{19}F NMR spectrum of ligand **6DFH** in d-acetone at 25 ℃.

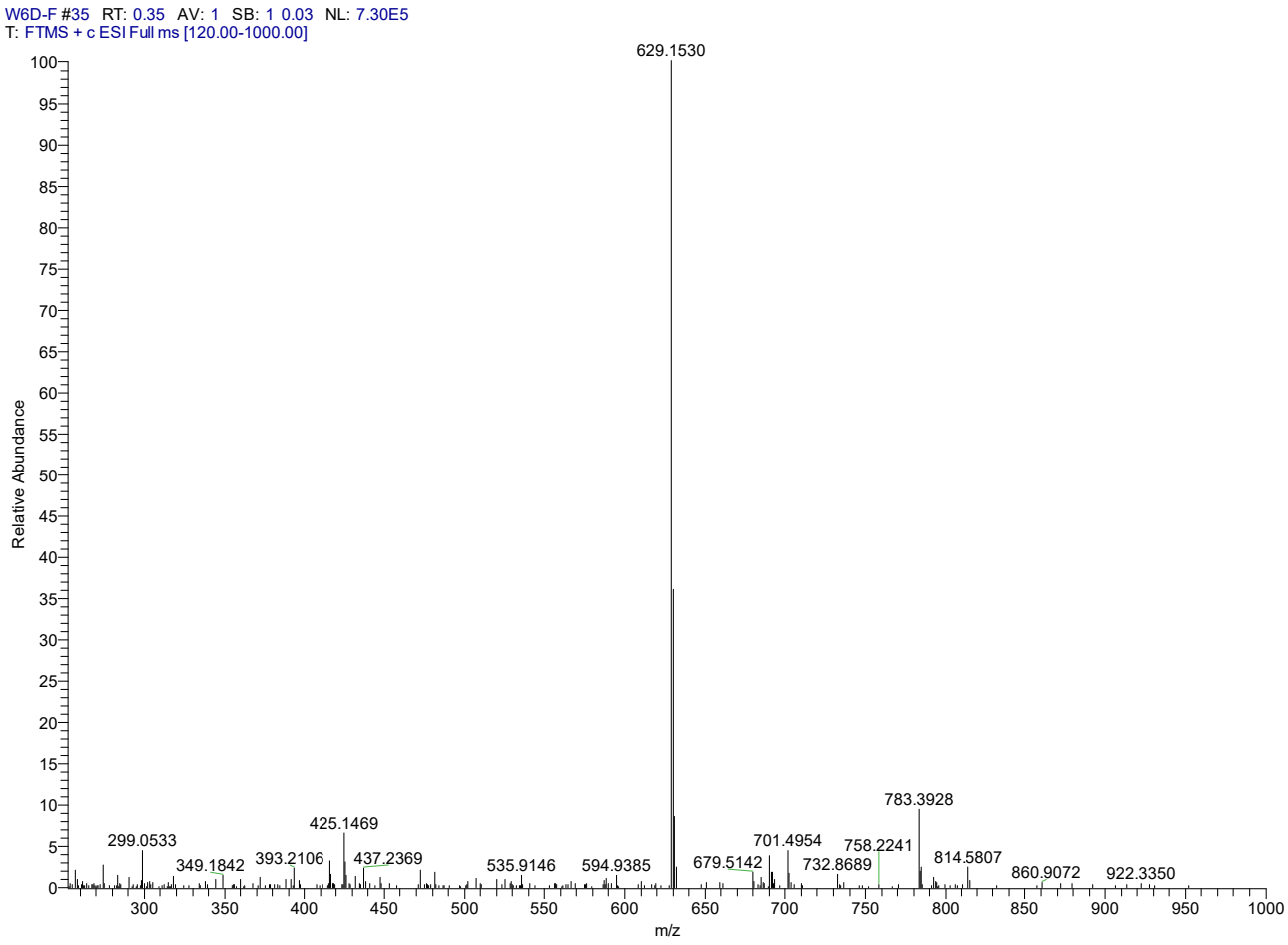


Figure S4. ESI-MS of ligand **6DFH** in methanol.

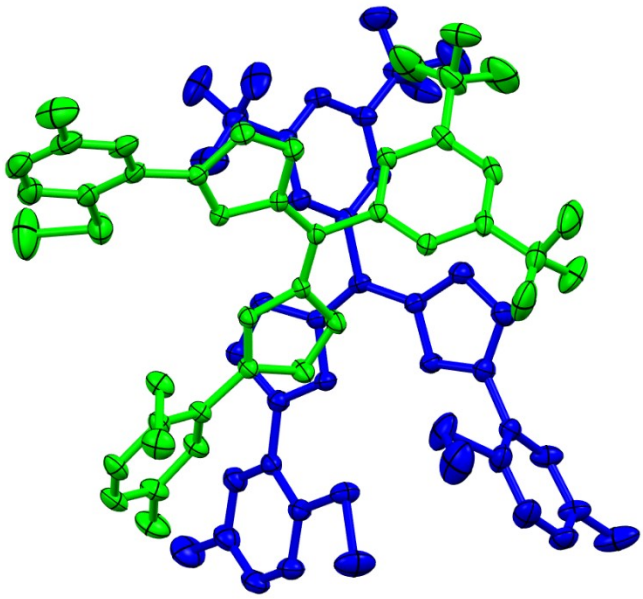


Figure S5. X-ray crystal structure of **6DFH** in the asymmetric unit shown at the 30% ellipsoid probability. All hydrogen atoms are omitted for clarity. The two units were distinguished by blue and green color.

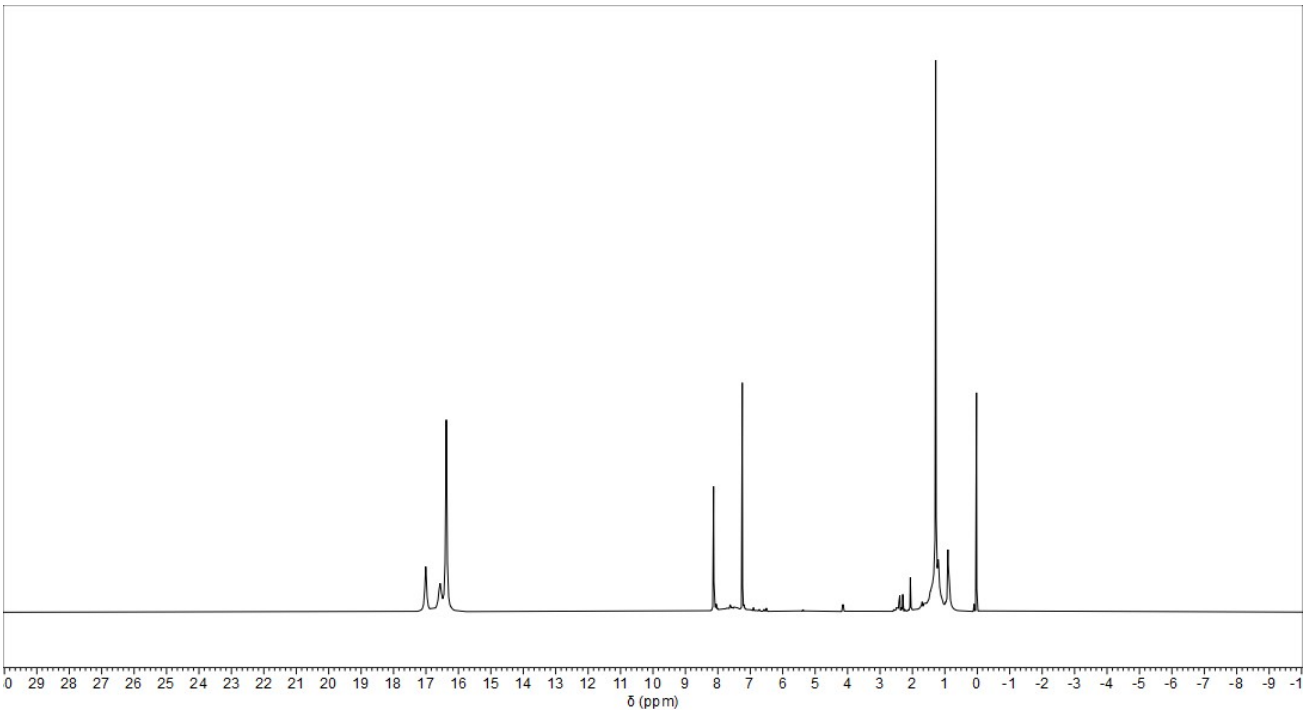


Figure S6. ^{1}H NMR spectra of complex **(6DFNiCl)$_2$** in $CDCl_3$ at 25 ℃.

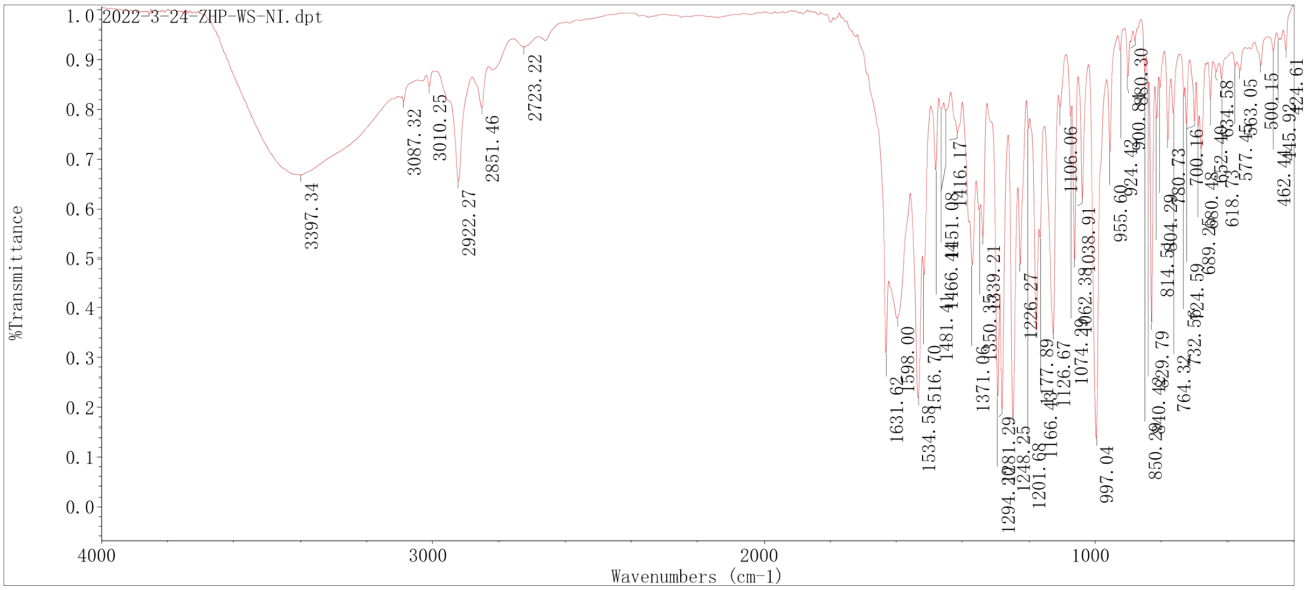


Figure S7. Infrared spectrum of complex **(6DFNiCl)$_2$** in solid state based on KBr.

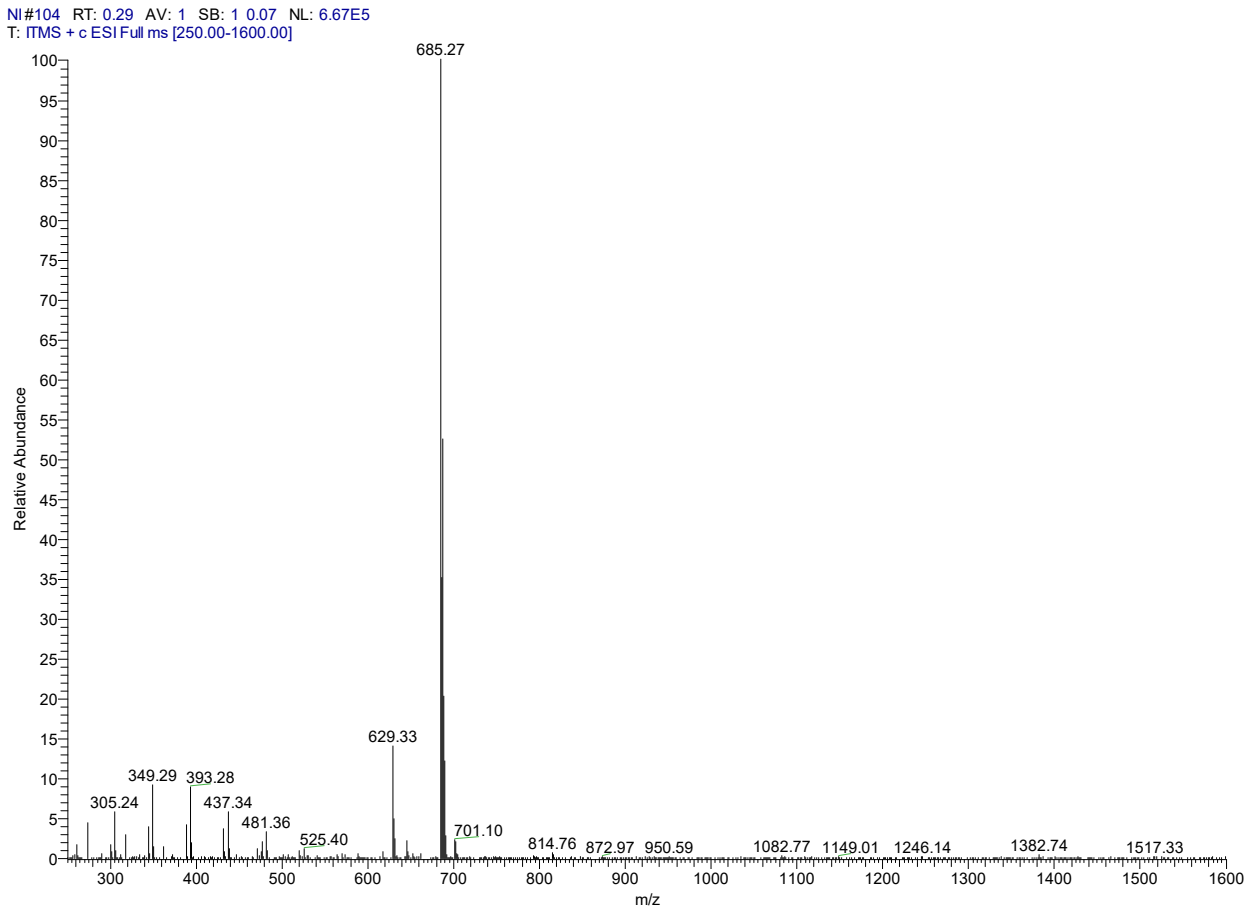


Figure S8. ESI-MS of complex **(6DFNiCl)$_2$** in CH_2Cl_2. Peak attribution (m/z): 685.27: 6DFNi ($C_{33}H_{25}N_2S_2F_6Ni$).

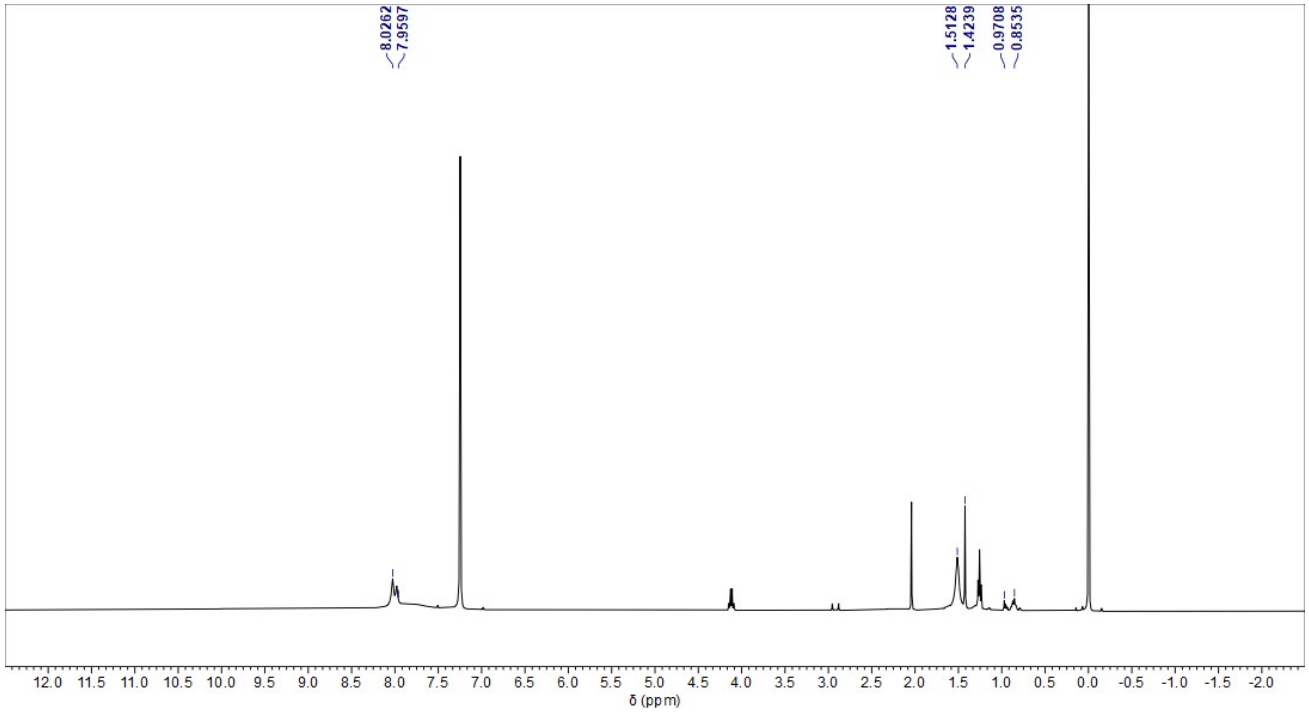


Figure S9. ^{1}H NMR spectra of complex **6DFCuCl** in $CDCl_3$ at 25 °C.

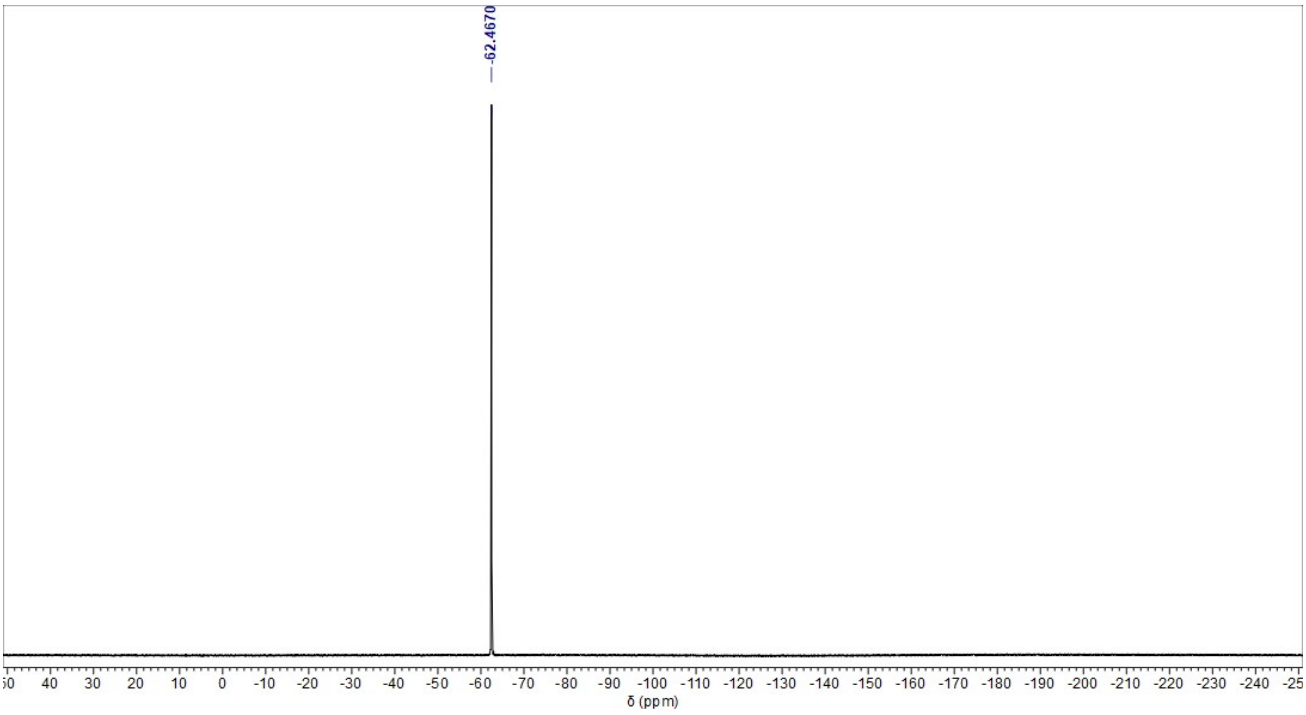


Figure S10. ^{19}F NMR spectra of ligand **6DFCuCl** in d-acetone at 25 °C.

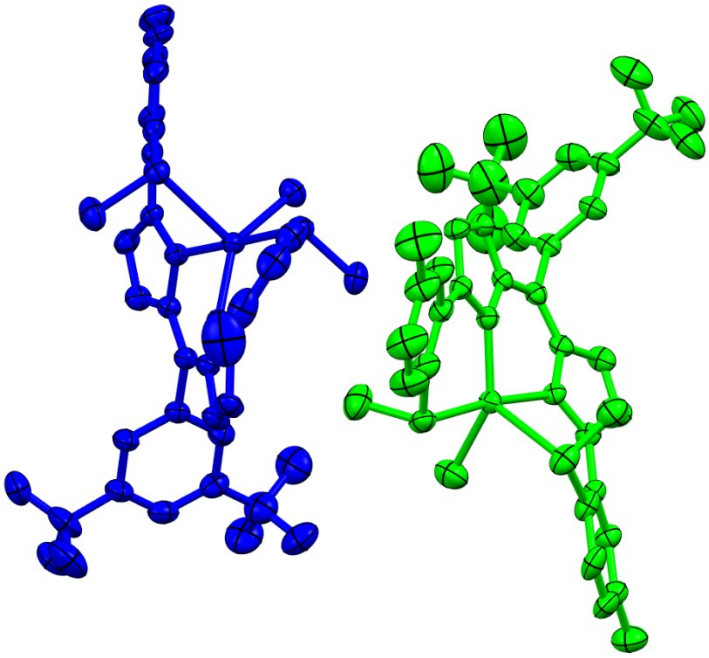


Figure S11. X-ray crystal structure of **6DFCuCl** in the asymmetric unit shown at the 30% ellipsoid probability. All hydrogen atoms are omitted for clarity. The two units were distinguished by blue and green color.

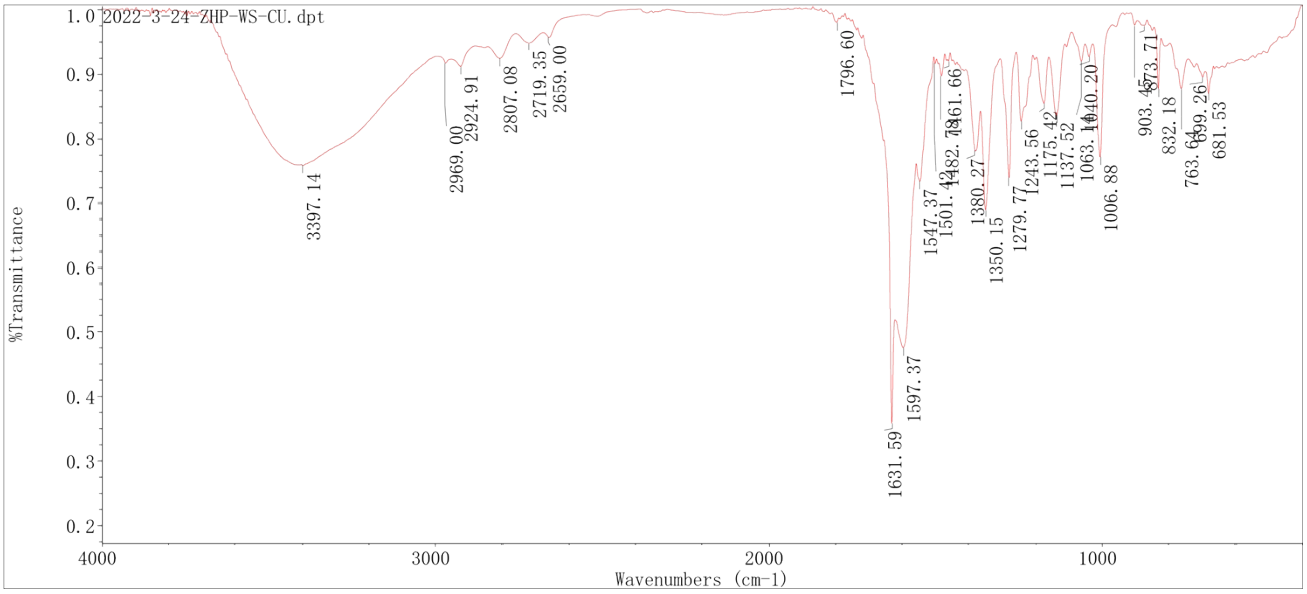


Figure S12. Infrared spectrum of complex **6DFCuCl** in solid state based on KBr.

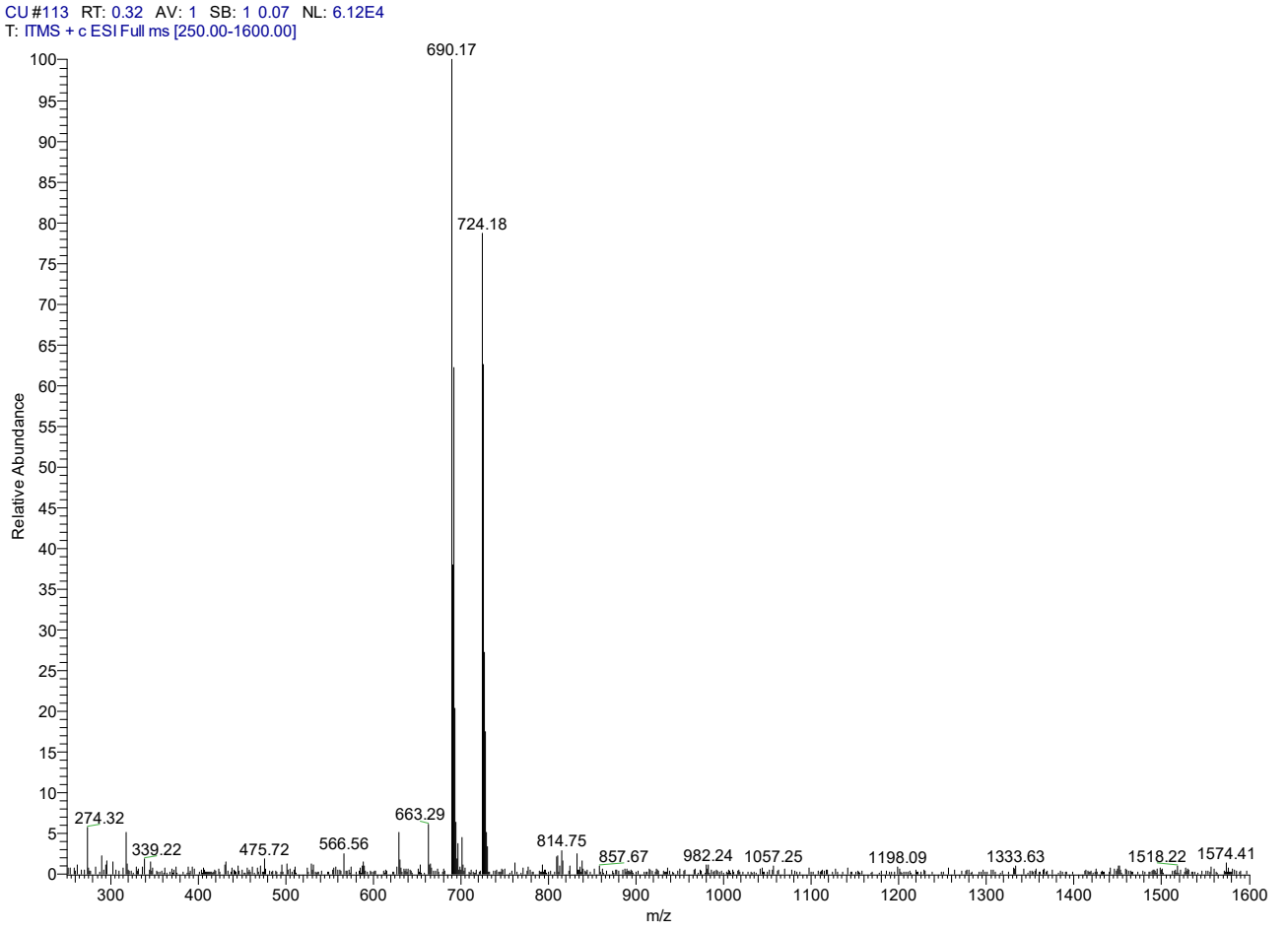


Figure S13. ESI-MS of complex **6DFCuCl** in CH_2Cl_2. Peak attribution (m/z): 690.17: 6DFCu ($C_{33}H_{25}N_2S_2F_6Cu$).

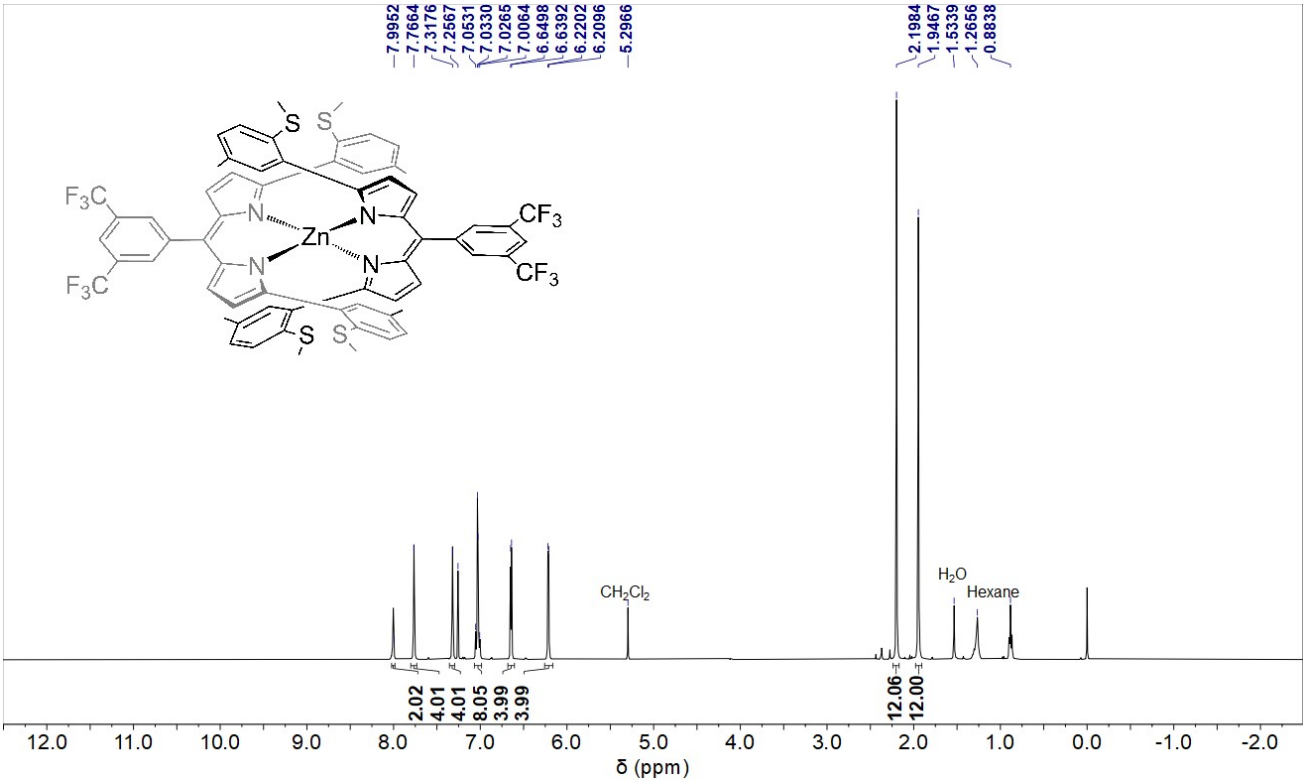


Figure S14. ^{1}H NMR spectra of complex **$(6DF)_2Zn$** in $CDCl_3$ at 25 °C.

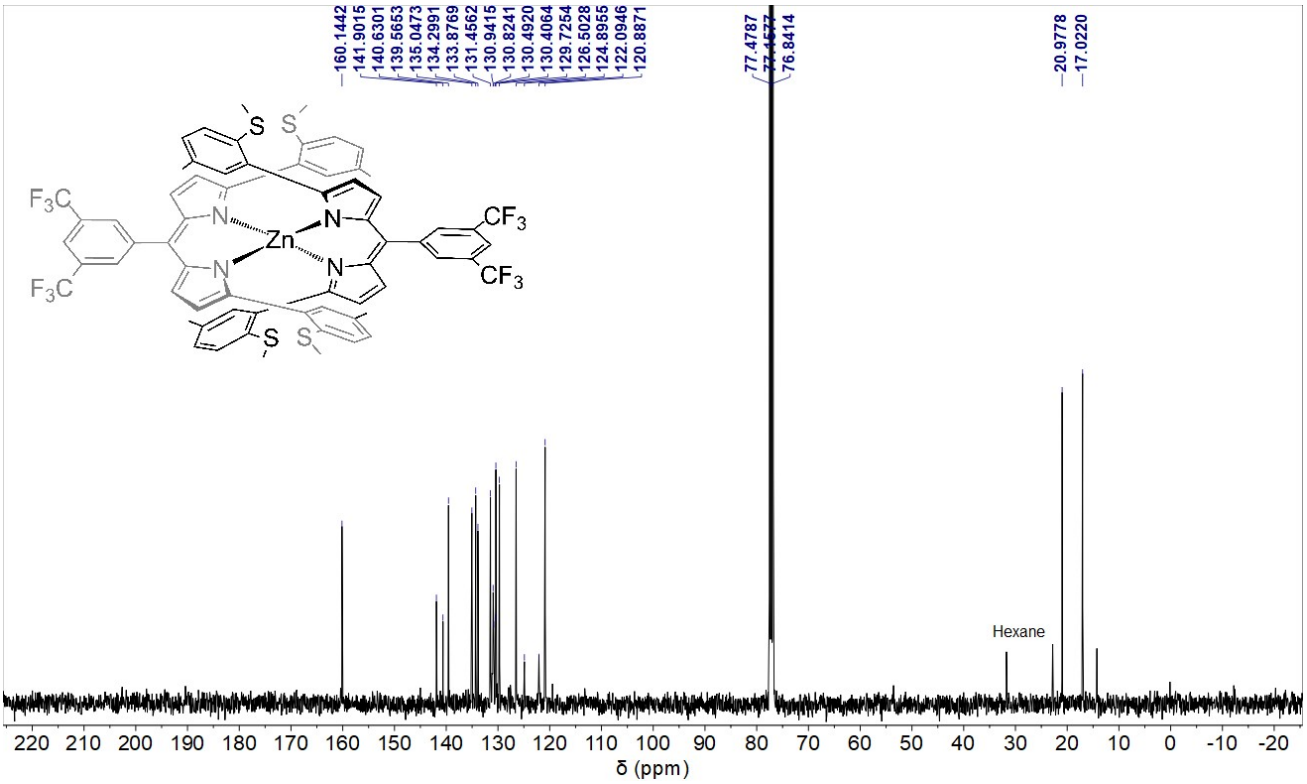


Figure S15. ^{13}C NMR spectra of complex **$(6DF)_2Zn$** in $CDCl_3$ at 25 °C.

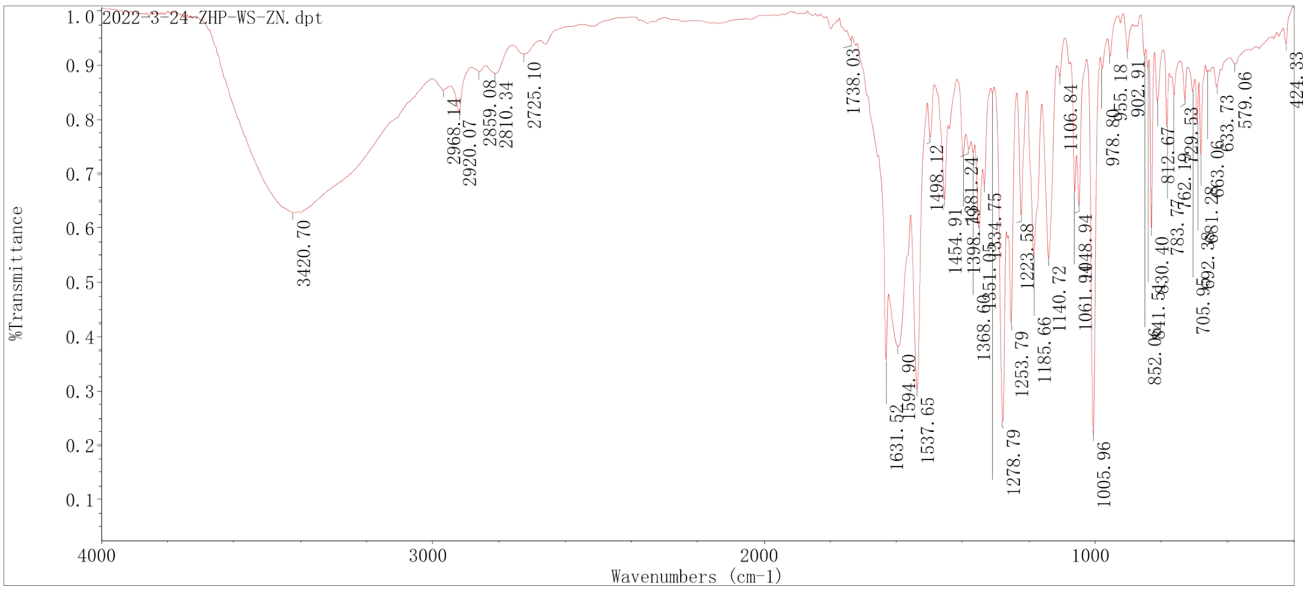


Figure S16. Infrared spectrum of complex **(6DF)$_2$Zn** in solid state based on KBr.

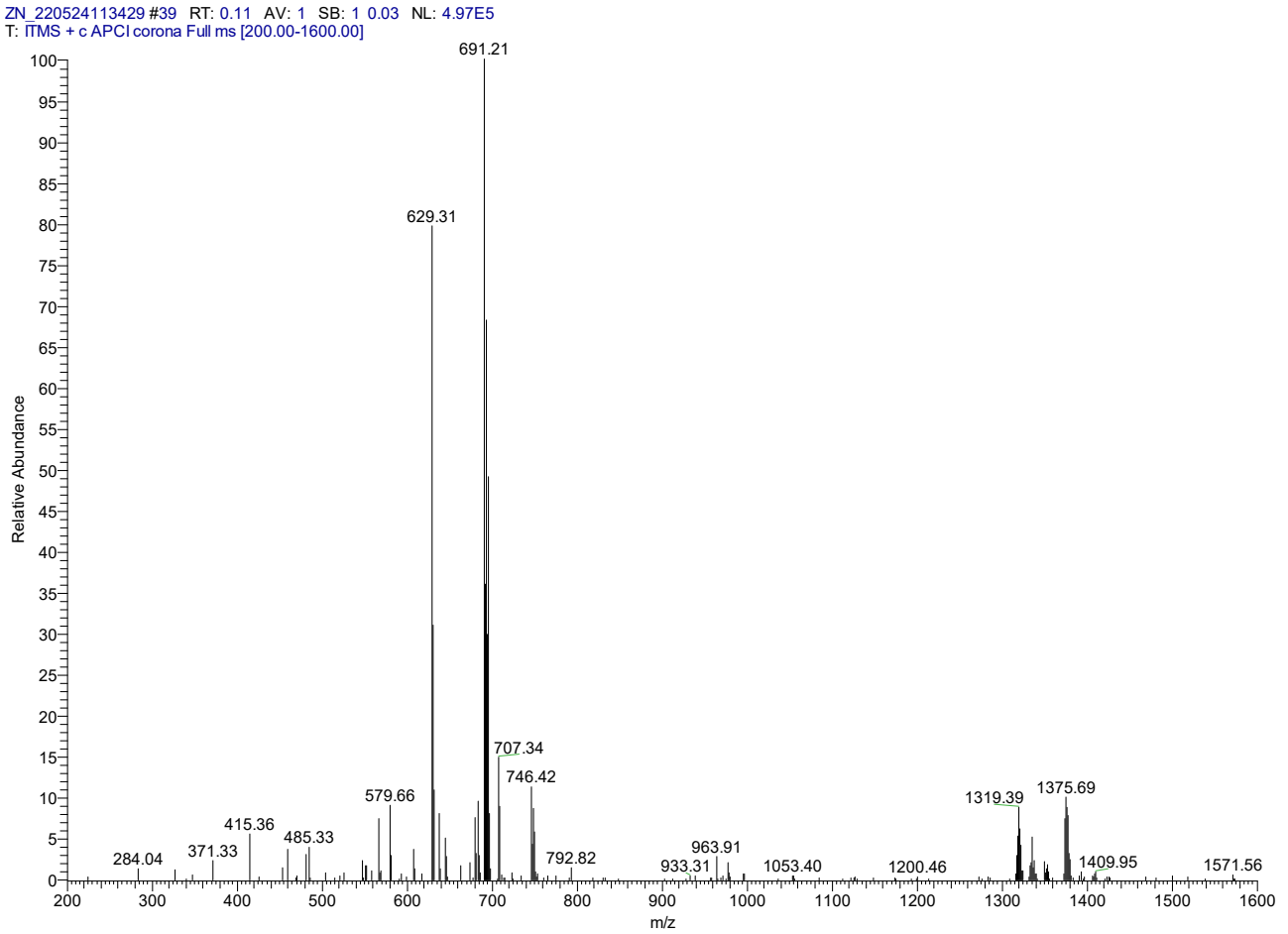


Figure S17. APCI-MS of **(6DF)$_2$Zn** in CH_2Cl_2. Peak attribution (m/z): 629.31: 6DFH+H ($C_{33}H_{26}N_2S_2F_6$); 691.21: 6DFZn ($C_{33}H_{25}N_2S_2F_6Zn$).

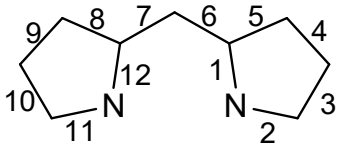
Table S1 Crystallographic data.

Identification code	**6DFH**	**$(6DFNiCl)_2$**	**6DFCuCl**	**$(6DF)_2Zn$**
Empirical formula	$C_{33}H_{26}F_6N_2S_2$	$C_{66}H_{50}Cl_2F_{12}N_4Ni_2S_4$	$C_{33}H_{25}ClCuF_6N_2S_2$	$C_{66}H_{50}F_{12}N_4S_4Zn$
Formula weight	628.68	1443.66	726.66	1320.71
Temperature/K	296.15	296.15	296.15	296.15
Crystal system	monoclinic	triclinic	triclinic	orthorhombic
Space group	$P2_1/c$	P-1	P-1	$P2_12_12_1$
a/Å	9.5425(14)	10.3025(17)	16.2289(19)	13.5949(13)
b/Å	22.706(3)	12.284(2)	16.6073(19)	17.6861(17)
c/Å	28.330(4)	14.517(2)	17.416(2)	28.194(3)
α/°	90	69.290(2)	69.500(2)	90
β/°	93.511(2)	70.236(2)	69.628(2)	90
γ/°	90	85.129(3)	62.269(2)	90
Volume/Å^3	6126.8(15)	1616.1(5)	3793.4(8)	6779.0(11)
Z	8	1	4	4
ρ_{calc} g/cm^3	1.363	1.483	1.272	1.294
μ/mm^{-1}	0.236	0.873	0.808	0.559
F(000)	2592.0	736.0	1476.0	2704.0
Crystal size/mm^3	0.32 × 0.25 × 0.18	0.18 × 0.16 × 0.08	0.31 × 0.25 × 0.12	0.22 × 0.21 × 0.1
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.88 to 55.004	3.178 to 49.994	2.908 to 49.998	2.718 to 50
Index ranges	-12 ≤ h ≤ 12, -29 ≤ k ≤ 27, -35 ≤ l ≤ 33	-12 ≤ h ≤ 12, -14 ≤ k ≤ 13, -17 ≤ l ≤ 16	-18 ≤ h ≤ 19, -19 ≤ k ≤ 19, -20 ≤ l ≤ 20	-16 ≤ h ≤ 12, -21 ≤ k ≤ 21, -33 ≤ l ≤ 33
Reflections collected	49056	11770	27615	49426
Independent reflections	13068 [Rint = 0.0611, Rsigma = 0.0587]	5658 [Rint = 0.0529, Rsigma = 0.0934]	13245 [Rint = 0.0331, Rsigma = 0.0536]	11937 [Rint = 0.0710, Rsigma = 0.0723]
Data/restraints/parameters	13068/293/903	5658/272/475	13245/726/967	11937/368/940
Goodness-of-fit on F^2	1.027	1.006	1.032	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0631	R_1 = 0.0545	R_1 = 0.0766	R1 = 0.0527
	wR_2 = 0.1596	wR_2 = 0.1150	wR_2 = 0.2147	wR2 = 0.1135
Final R indexes [all data]	R_1 = 0.1146	R_1 = 0.1081	R_1 = 0.1090	R1 = 0.0895
	wR_2 = 0.1915	wR_2 = 0.1385	wR_2 = 0.2412	wR2 = 0.1302
Largest diff. peak/hole / e Å^{-3}	1.11/-0.49	0.40/-0.37	2.45/-1.12	0.50/-0.24
Flack parameter				0.007(9)

Table S2. Selected bond lengths (Å) in the crystal structures of the Tetradentate N_2S_2 complexes.

$(6DFNiCl)_2$				**6DFCuCl**				**$(6DF)_2Zn$**			
Cl1	Ni1	Cl1[a]	81.95(4)	Cl1	Cu1	S1	86.48(8)	N1	Zn1	N2	96.67(19)
Cl11	Ni1	S1	92.89(5)	Cl1	Cu1	S2	100.53(8)	N1	Zn1	N3	111.4(2)
Cl1	Ni1	S1	89.59(5)	S1	Cu1	S2	87.80(7)	N1	Zn1	N4	115.7(2)
S2	Ni1	Cl1	168.27(5)	N1	Cu1	Cl1	143.95(16)	N2	Zn1	N3	118.3(2)
S2	Ni1	Cl1[a]	86.53(5)	N1	Cu1	S1	93.41(14)	N2	Zn1	N4	118.1(2)
S2	Ni1	S1	93.23(5)	N1	Cu1	S2	115.49(15)	N3	Zn1	N4	97.83(19)
N1	Ni1	Cl1[a]	173.69(11)	N2	Cu1	Cl1	92.64(15)				
N1	Ni1	Cl1	93.45(11)	N2	Cu1	S1	171.79(15)				
N1	Ni1	S1	82.73(11)	N2	Cu1	S2	84.34(15)				
N1	Ni1	S2	98.20(11)	N2	Cu1	N1	92.10(19)				
N2	Ni1	Cl1	94.61(11)	Cl2	Cu2	S3	85.89(7)				
N2	Ni1	Cl1[a]	98.01(11)	Cl2	Cu2	S4	107.11(7)				
N2	Ni1	S1	168.77(11)	S3	Cu2	S4	96.58(6)				
N2	Ni1	S2	84.74(11)	N3	Cu2	Cl2	93.15(15)				
N2	Ni1	N1	86.62(15)	N3	Cu2	S3	178.83(15)				
[a]1-X,1-Y,1-Z				N3	Cu2	S4	83.06(15)				
				N3	Cu2	N4	90.7(2)				
				N4	Cu2	Cl2	142.87(16)				
				N4	Cu2	S3	90.52(14)				
				N4	Cu2	S4	110.02(15)				

Table S3. Selected bond lengths (Å) of dipyrrins units in the crystal structures.



Bonds	**6DFH**	**$(6DFNiCl)_2$**	**6DFCuCl**	**$(6DF)_2Zn$**
1	1.383(3) /1.387(4)	1.393(6)	1.386(7) /1.384(7)	1.396(7) /1.399(7)
2	1.351(4) /1.353(4)	1.340(6)	1.352(7) /1.356(7)	1.354(8) /1.340(8)
3	1.403(4) /1.388(5)	1.439(6)	1.436(8) /1.418(9)	1.416(8) /1.434(9)
4	1.375(4) /1.383(5)	1.347(7)	1.346(9) /1.355(9)	1.347(9) /1.369(10)
5	1.404(4) /1.384(4)	1.427(6)	1.404(8) /1.426(8)	1.425(9) /1.408(9)
6	1.409(4) /1.431(4)	1.397(6)	1.407(8) /1.401(8)	1.396(9) /1.413(9)
7	1.396(4) /1.371(4)	1.397(6)	1.381(8) /1.379(8)	1.398(9) /1.388(8)
8	1.432(4) /1.443(4)	1.420(7)	1.418(8) /1.432(8)	1.424(9)/ 1.431(9)
9	1.335(4) /1.347(4)	1.370(7)	1.359(9) /1.346(9)	1.375(10)/ 1.360(9)
10	1.359(4) /1.446(4)	1.426(7)	1.423(9) /1.410(8)	1.422(9)/ 1.420(9)
11	1.335(4) /1.319(4)	1.343(6)	1.342(7) /1.340(7)	1.355(8) /1.338(7)
12	1.391(3) /1.401(3)	1.387(5)	1.402(7) /1.391(7)	1.388(7) /1.413(7)