Supporting Information

See-Saw Ni(II) thiosemicarbazones, Energy and Photophysical Properties

Satyendra Verma,[a] Jitendra Nath,[b] Jubaraj B. Baruah[a]*

Content list

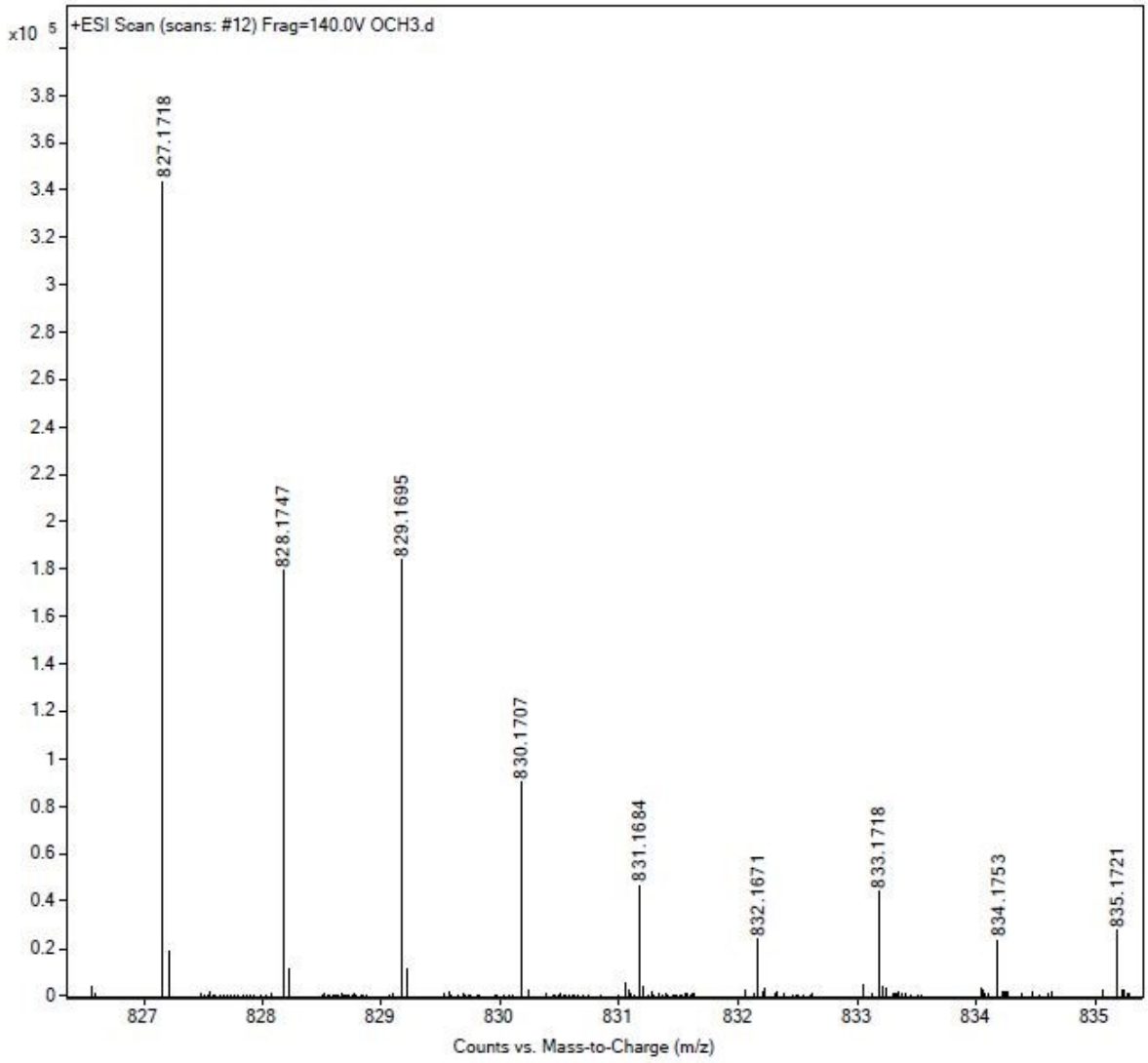


Figure 1S: High-resolution mass of the complexes **1** (inset has the respective calculated mass pattern).

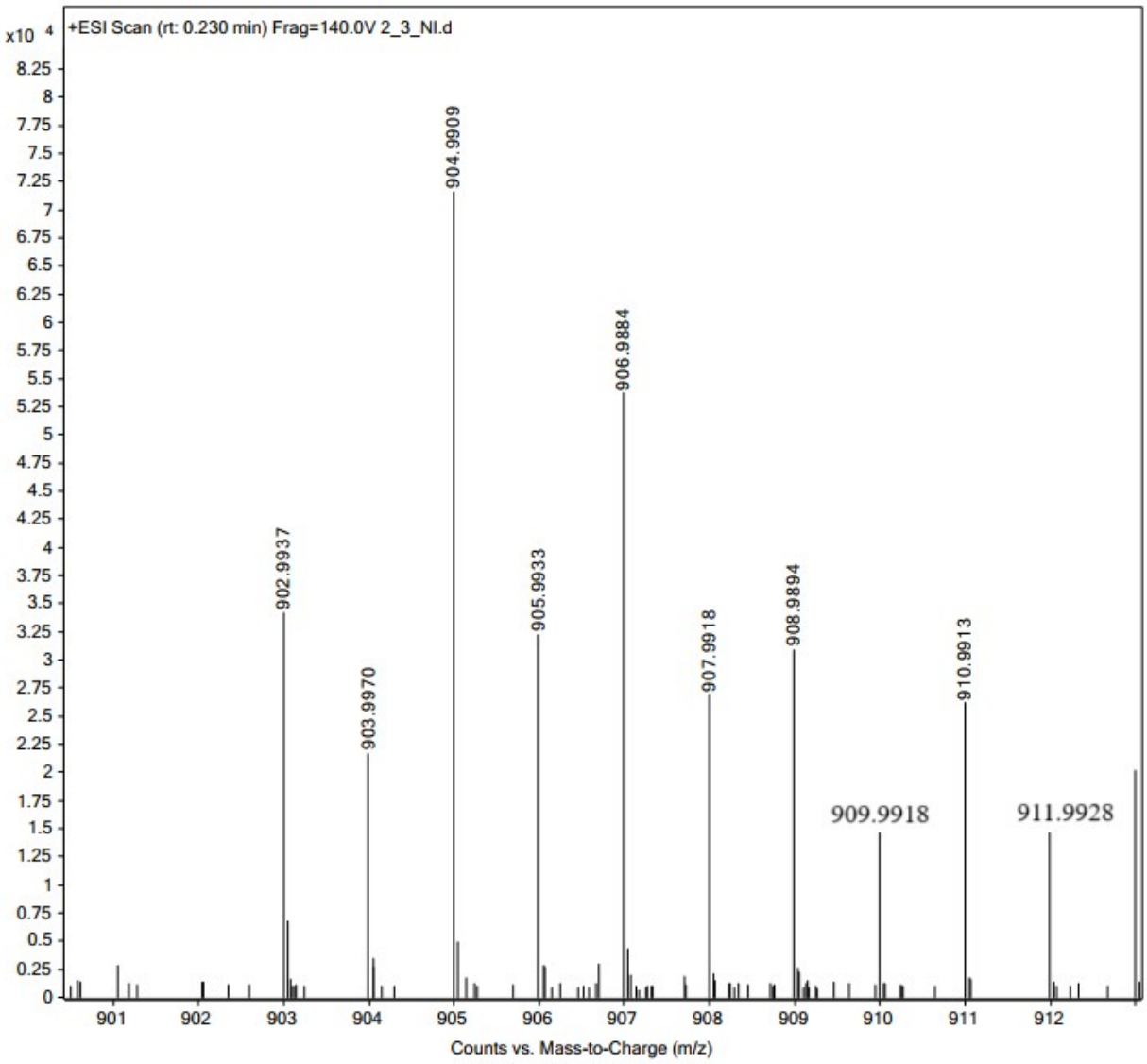
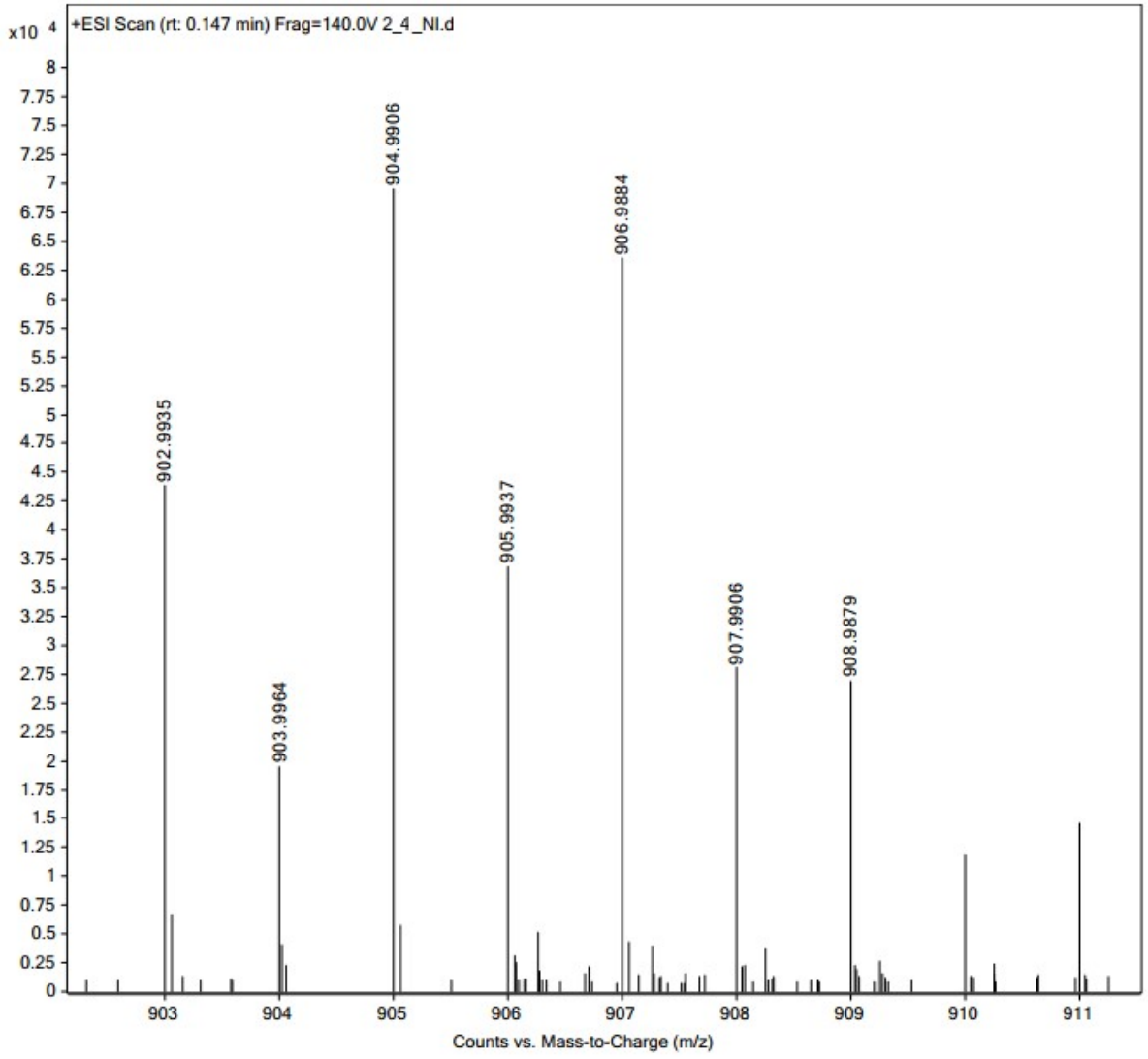
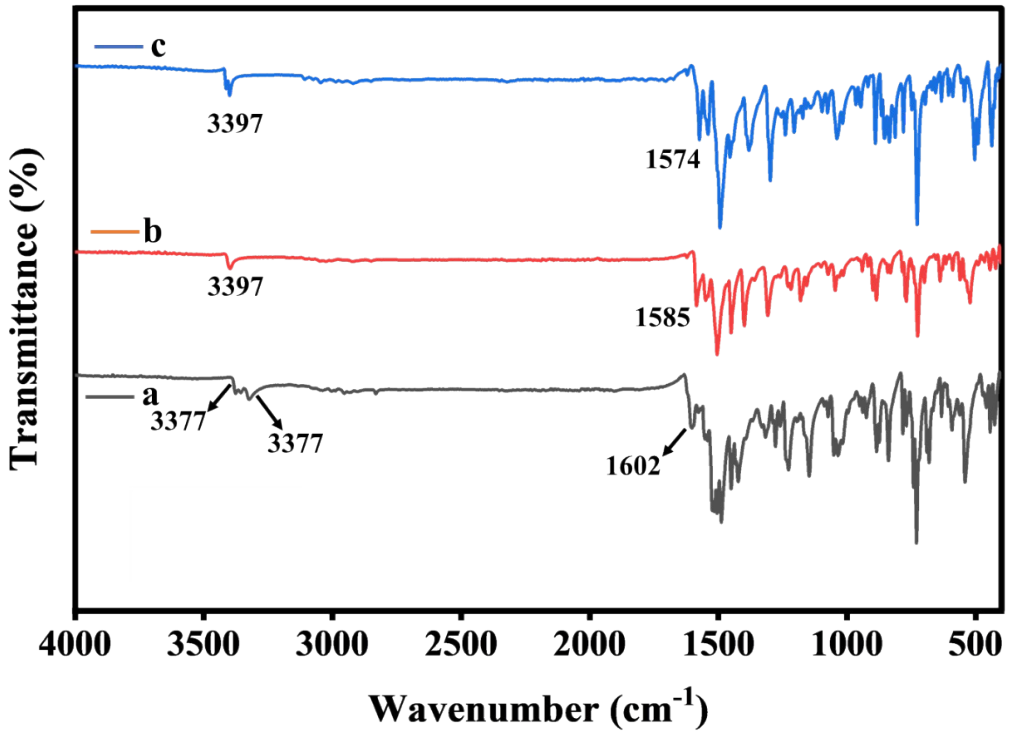


Figure 2S: High-resolution mass of the complexes **2** (inset has the respective calculated mass pattern).

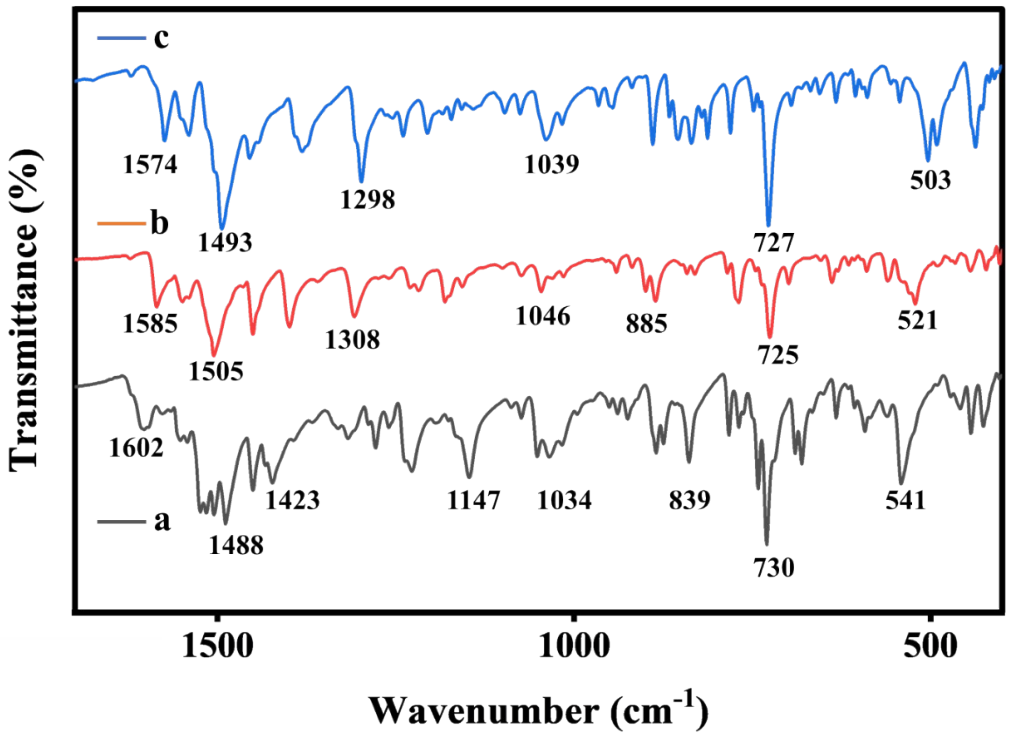


(c)

Figure 3S: High-resolution mass of the complexes **3** (inset has the respective calculated mass pattern).


c
3397
1574
b
3397
1585
a
3377
3377
1602
Transmittance (%)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

(a)


c
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1298
1039
727
503
b
1585
1505
1308
1046
885
725
521
1602
1488
1423
1147
1034
839
730
541
a
1500
1000
500
Wavenumber (cm-1)
Transmittance (%)

(b)

Figure 4S: IR spectra of the nickel complexes (a) complex **1**, (b) complex **2**, and (c) complex **3** (on the right side is the expanded region showing peaks appearing between 500-1500 cm^{-1}.

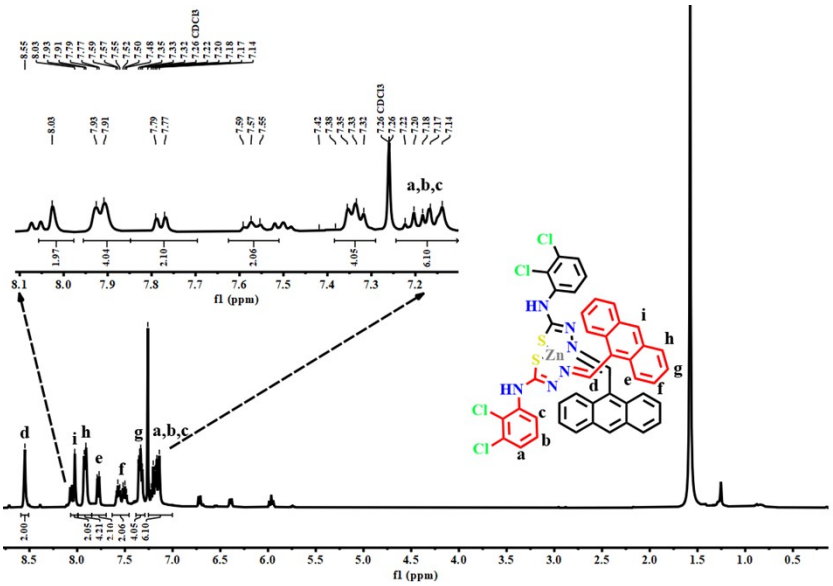


Figure 5S: ^{1}HNMR (400 MHz, $CDCl_3$) spectra of Complex **2**

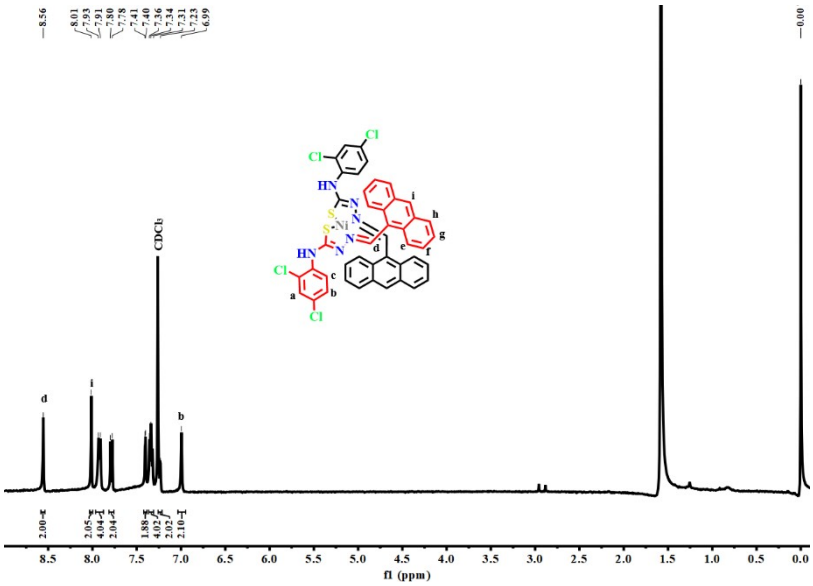


Figure 6S: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of Complex **3**

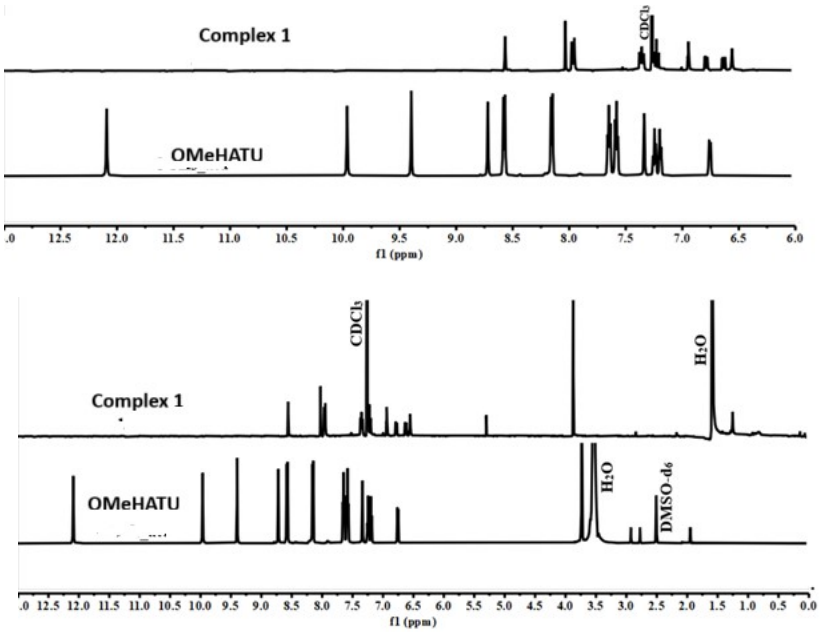


Figure 7S: Comparison ^{1}H NMR (400 MHz, $CDCl_3$/ DMSO-d_6) spectra of Ligand OMeHATU and complex **1** (Top is expanded spectra).

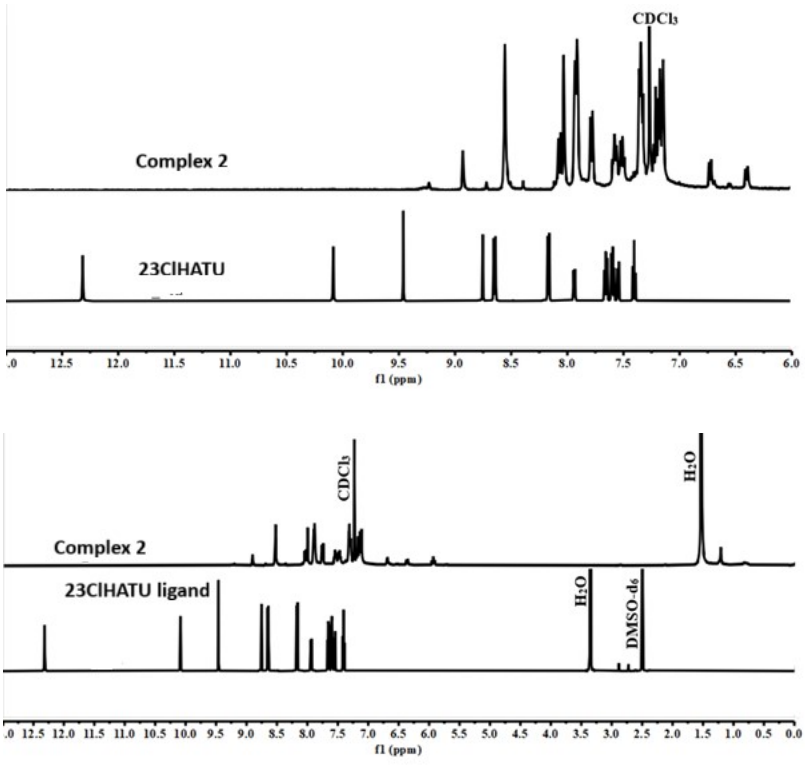
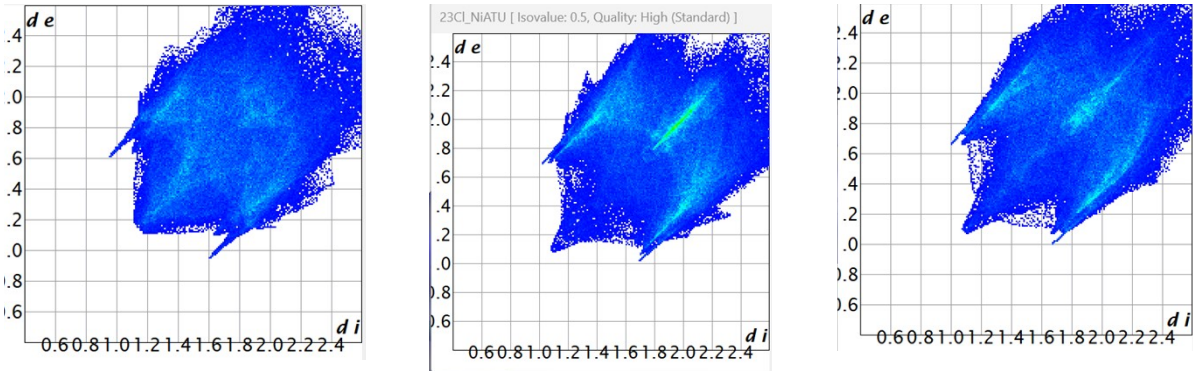


Figure 8S: Comparison ^{1}HNMR (400 MHz, $CDCl_3$/ DMSO-d_6) spectra of 23ClHATU ligand and complex **2** (on top expanded aromatic region).



(a) **(b)** **(c)**

Figure 9S: Fingerprint plots from the Hirshfeld analyses of the complexes (a) **1**, (b) **2**, and (c) **3**.

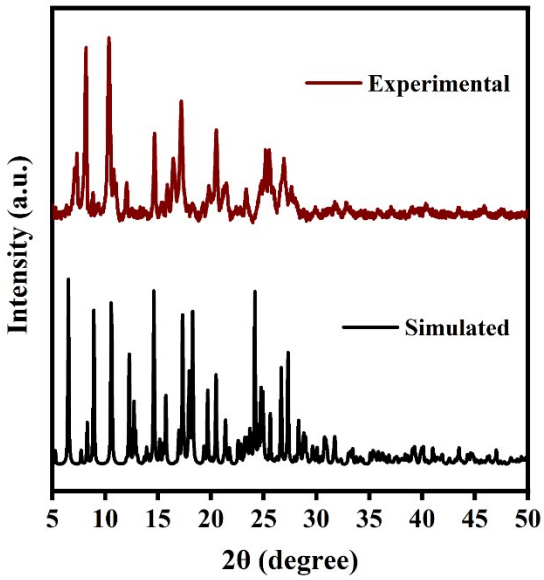


Figure 10S**:** Powder XRD patterns of $Ni(23ClATU)_2$ (complex **2**)

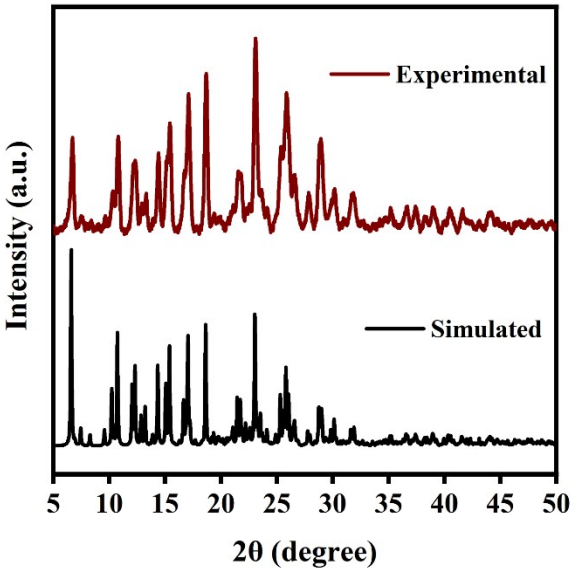


Figure 11S: Powder XRD patterns of $Ni(24ClATU)_2$ (Complex **3**)

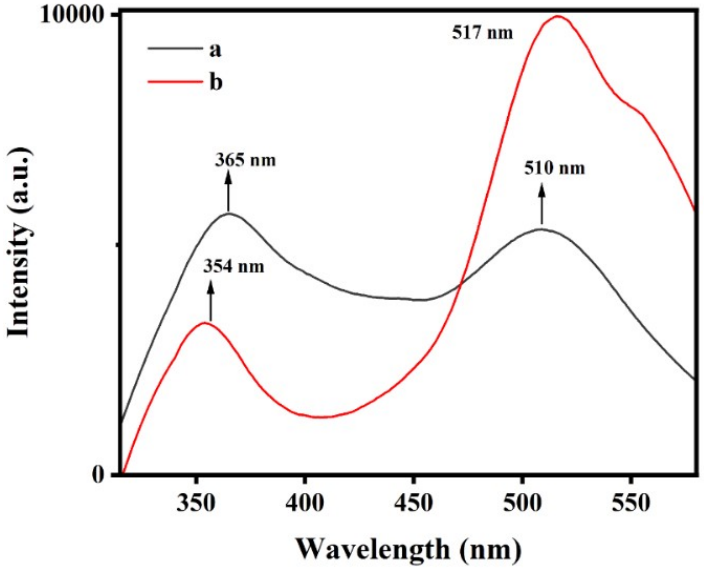


Figure 12S: Comparison of the dual emissions of the complexes **2** and **3** recorded in $CHCl_3$ (λ_{ex} = 300 nm, concentration 200 μM)

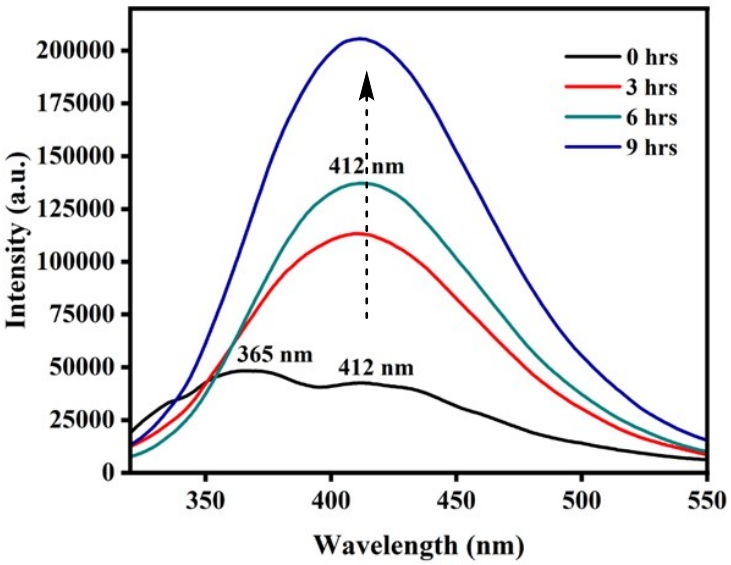


Figure 13S: Time-dependent fluorescence spectra Ni(3OMeATU)$_2$ (Complex **1**) (λ_{ex} = 300 nm, solvent $CHCl_3$, concentration 3.3 µM).

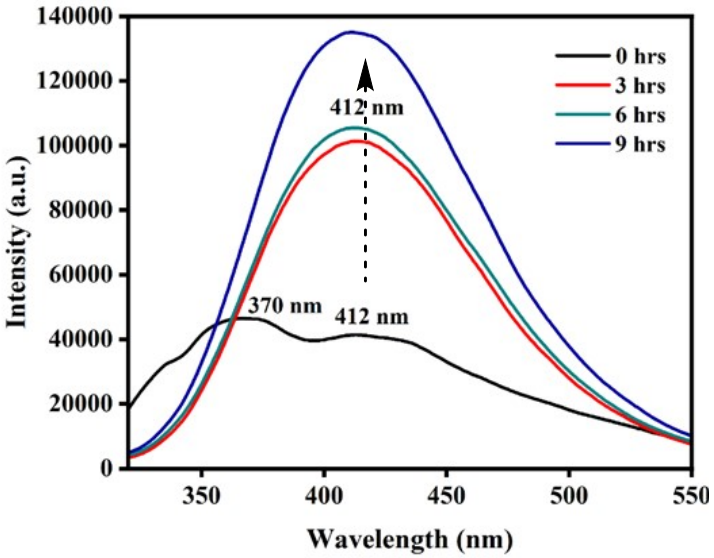


Figure 14S: Time-dependent fluorescence spectra Ni(23ClATU)$_2$ (complex **2**) (λ_{ex} = 300 nm, solvent $CHCl_3$, concentration 3.3 µM)

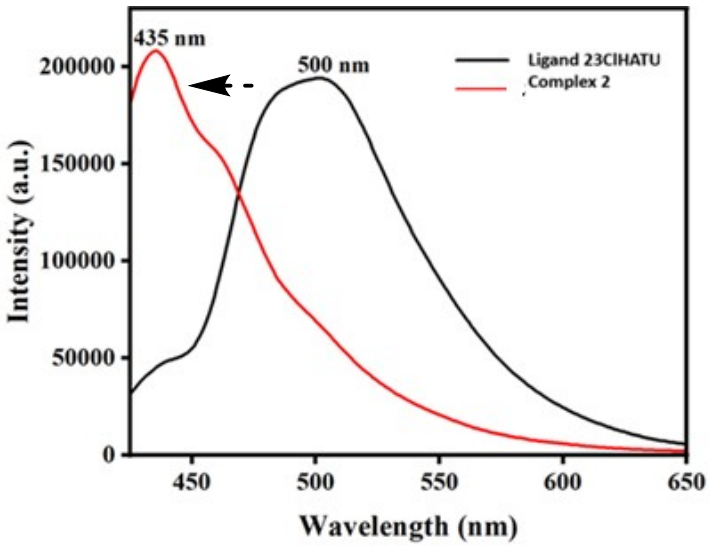


Figure 15S: Comparison of fluorescence spectra of (a) 23ClHATU (ligand) and (b) complex **2**, Ni(23ClATU)$_2$ in $CHCl_3$ (λ_{ex}= 400 nm, solvent $CHCl_3$, concentration 3.3 µM))

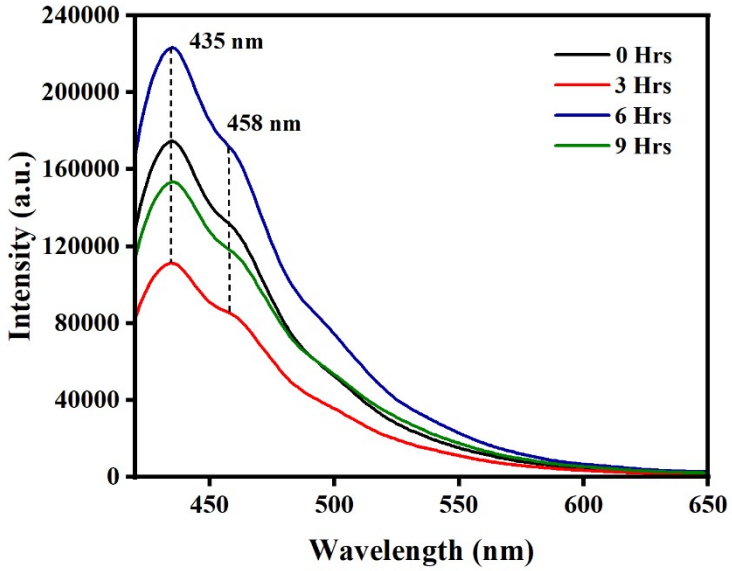


Figure 16S: Time-dependent fluorescence spectra complex **1**, Ni(3OMeATU)$_2$ (λ_{ex} = 400 nm, solvent $CHCl_3$, concentration 3.3 µM)

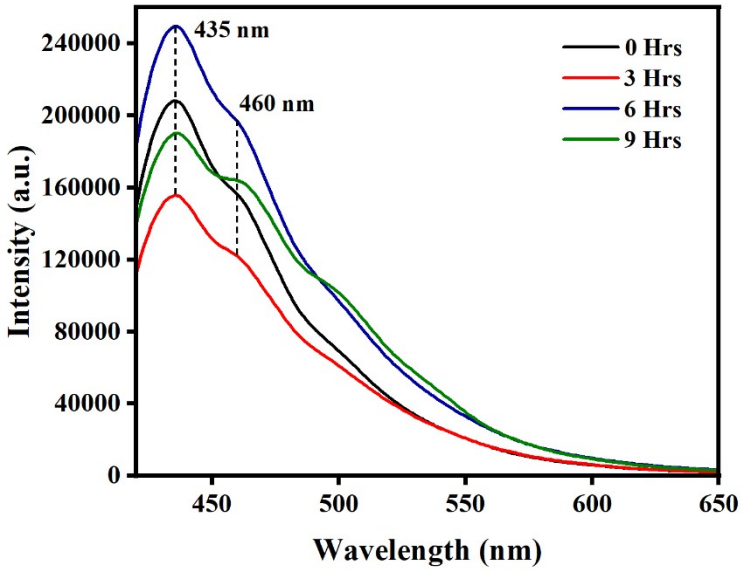


Figure 17S: Time-dependent fluorescence spectra Ni(24ClATU)$_2$ (complex **3**) (λ_{ex}= 400 nm solvent $CHCl_3$, concentration 3.3 µM)

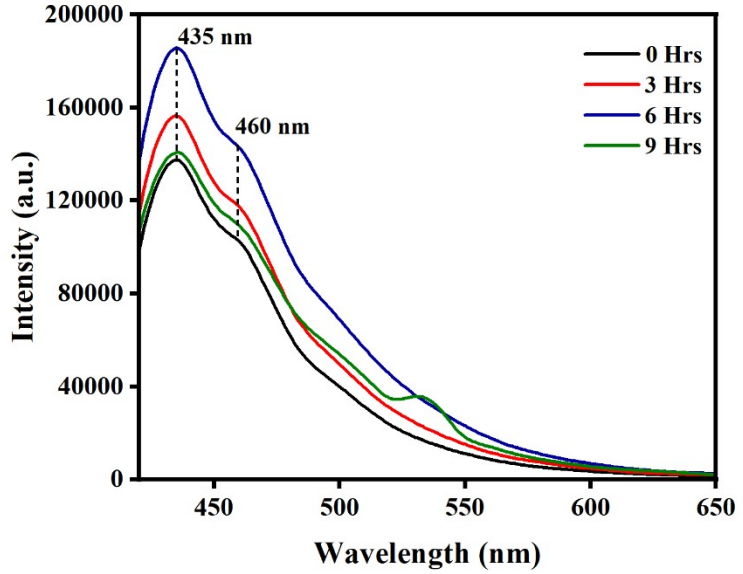


Figure 18S: Time-dependent fluorescence spectra Ni(23ClATU)$_2$ (complex **2**) (λ_{ex}= 400 nm, solvent $CHCl_3$, concentration 3.3 µM)

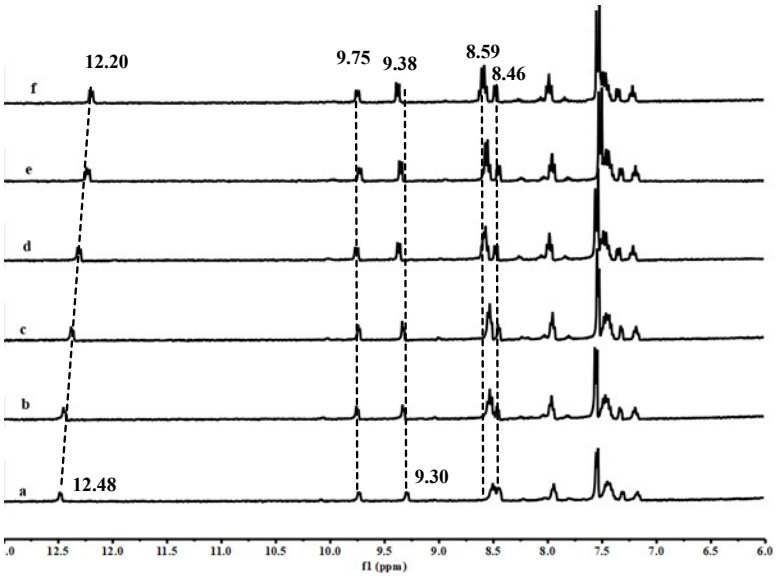


Figure 19S: Variable temperature ^{1}H NMR (400 MHz, $CDCl_3$: DMSO-d_6 1:1) spectra of ligand 24ClHATU. (a, b, c, d, e, f at -20, -10, 0, 10, 20, 25, respectively)

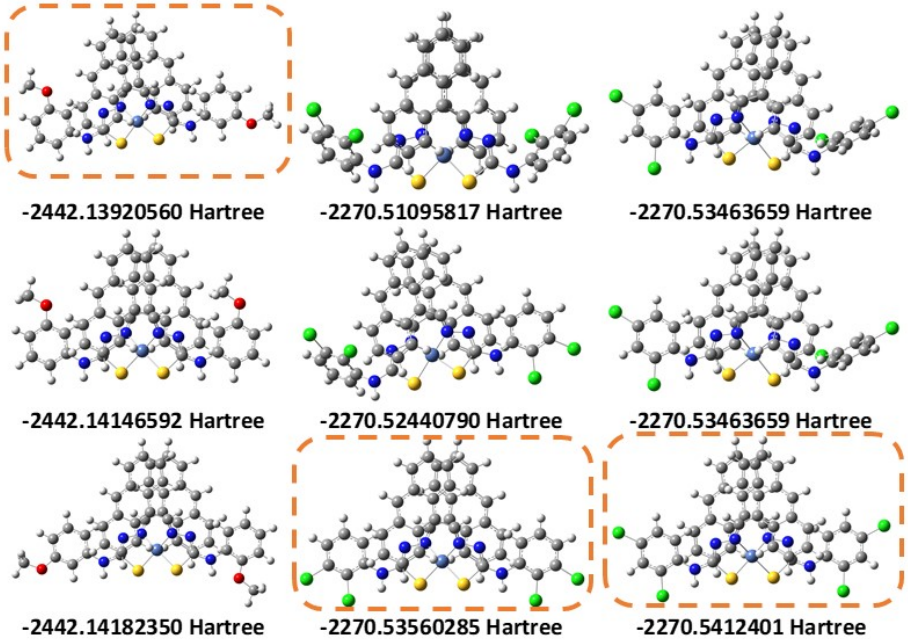


Figure 20S: The dispersion corrected energy associated with the isomers of the complexes **1-3**, the observed form is highlighted by encircled dots

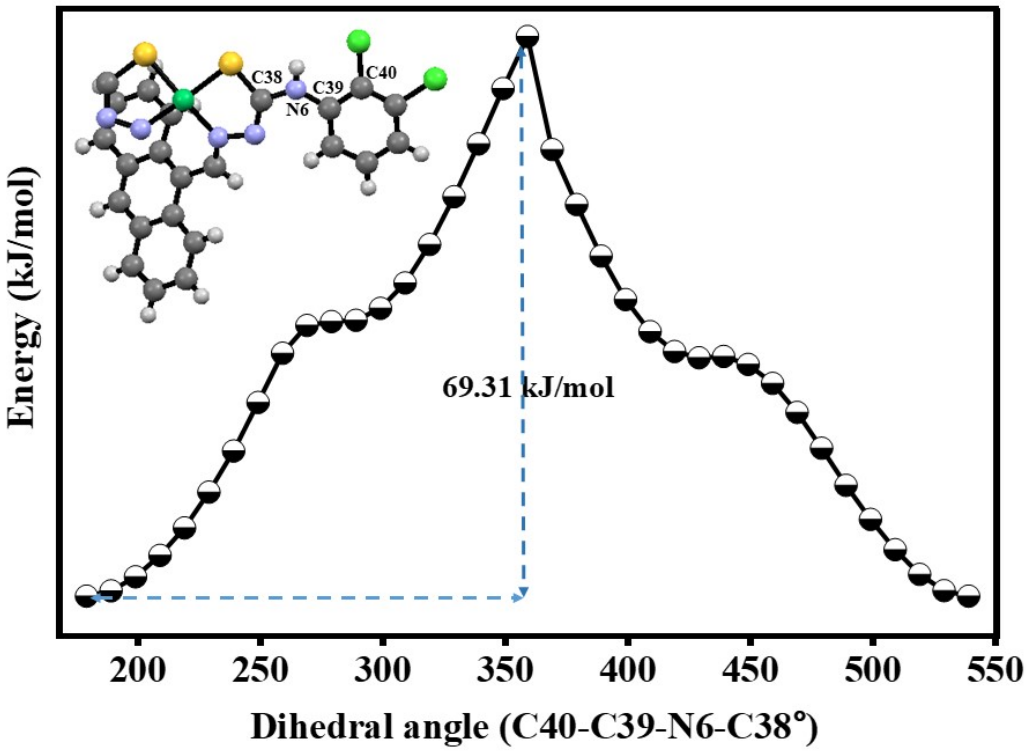


Figure 21S: Theoretically calculated change in the energy of complex **2** with different dihedral angles C40-C39-N6-C38. Calculations were done by DFT at the B3LYP functional level using LANL2DZ as the basis set

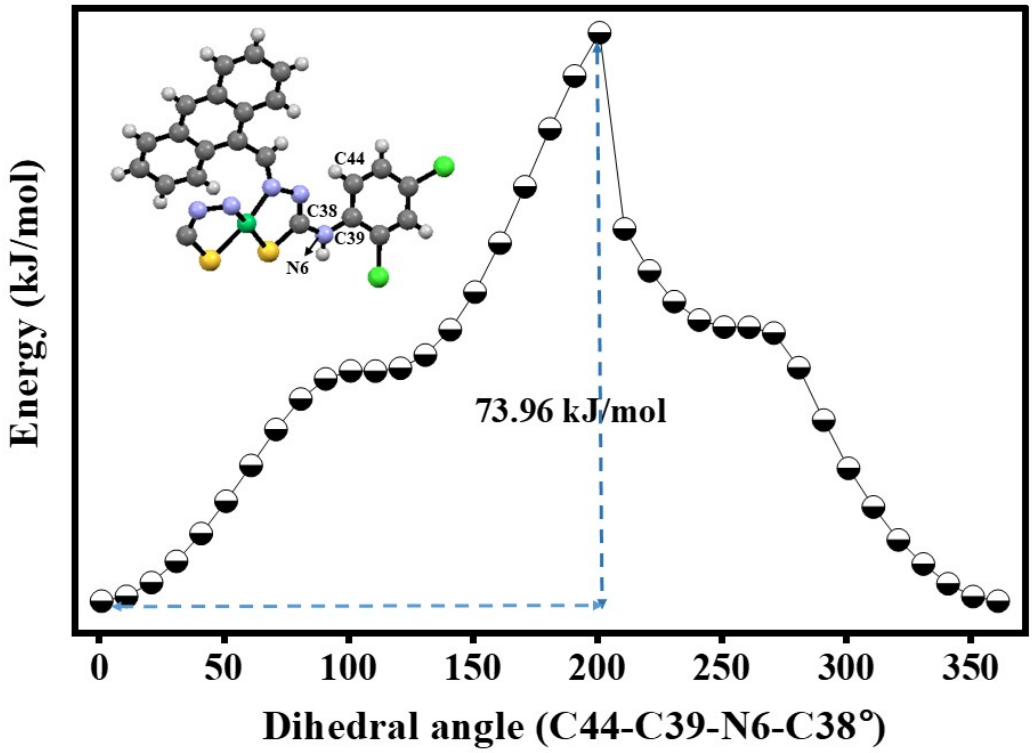
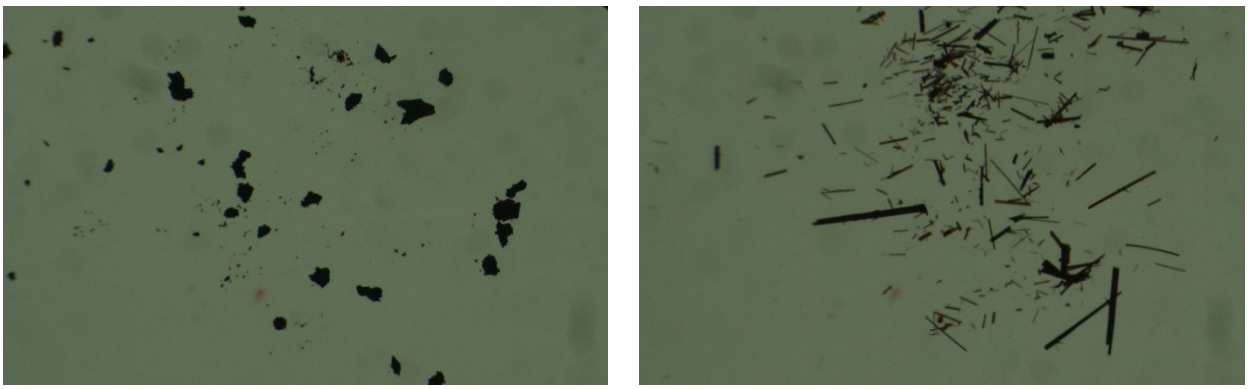


Figure 22S: Theoretically calculated change in the energy of complex **3** with different dihedral angles C44-C39-N6-C38. Calculations were done by DFT at the B3LYP functional level using LANL2DZ as the basis set



(a) (b)

Figure 23S: Microscopic images of crystals (a) complex **1** and (b) complex **2**

Table 1S: Crystal and refinement data of the complexes

Parameter	Complex **1**	Complex **2**	Complex **3**
Formula	$C_{46}H_{36}N_6O_2S_2Ni$	$C_{45}H_{29}N_6Cl_7S_2Ni$	$C_{44}H_{28}N_6S_2Cl_4Ni$
Mol. wt.	827.64	1024.72	905.35
Space group	*Pbca*	$P2_1/n$	$P2_1/c$
a(Å)	11.0335(4)	7.6501(14)	13.4028(16)
b(Å)	21.1887(8)	27.110(5)	25.516(3)
c (Å)	33.5173(13)	21.294(4)	11.7627(14)
α (°)	90	90	90
β (°)	90	90.173(6)	91.750(4)
γ (°)	90	90	90
V (Å^3)	7835.9(5)	4416.2(14)	4020.8(8)
Density, g cm^{-3}	1.403	1.541	1.496
Abs. coeff., mm^{-1}	0.650	0.999	0.894
F(000)	3440	2080	1848
Total no. of reflections	6884	7582	7108
Reflections, I > 2σ(I)	4206	3991	4834
Max. θ/°	24.998	24.8	25.049
Ranges (h, k, l)	-13 ≤ h13	−9≤ h ≤ 9	−15 ≤ h ≤ 15
	25 ≤ k ≤25	−31 ≤ k ≤31	−30 ≤ k≤ 30
	-39 ≤l ≤ 39	−23 ≤1 ≤ 25	−13 ≤ 1 ≤ 14
Completeness to 2θ (%)	99.9	99.9	99.9
Data/restraints/parameters	6884/2/516	7582/0/550	7108/0/514
GooF (F^2)	1.042	1.032	1.059
R indices [I > 2σ(I)]	0.0611	0.0785	0.0440
wR_2 [I > 2σ(I)]	0.1314	0.1685	0.0862
R indices (all data)	0.1175	0.1634	0.0798
wR_2 [all data]	0.1519	0.2015	0.0948
CCDC No.	2346244	2346249	2346251

Table 2S: Hydrogen bond parameters of the complexes

Compounds	D-H···A	$d_{D\text{-}H}$ (Å)	$d_{H\cdots A}$ (Å)	$d_{D\cdots A}$ (Å)	∠D-H···A (°)
Complex 1	N(6) –H(6)...S(1) [1/2+x,y,1/2-z]	0.93	2.71	3.539(4)	162
	C(2) –H(2)...N(1) [x,y,z]	0.93	2.55	3.066(6)	115
	C(22) –H(22)...N(2)[x,y,z]	0.93	2.33	2.937(6)	122
	C(35) –H(35)...N(4) [x,y,z]	0.93	2.54	3.086(5)	118
	C(41) –H(41)...N(5) [x,y,z]		2.34	2.926(6)	121
Complex 2	N(3) –H(3)...Cl(1) [x,y,z]	0.86	2.44	2.911(6)	115
	N(3) –H(6)...Cl(3) [x,y,z]	0.86	2.45	2.91 (6)	115
	C(12) –H(12)…N(1) [x,y,z]	0.93	2.51	3.055(9)	118
	C(22) –H(22)...N(2) [x,y,z]	0.93	2.28	2.891(4)	122
	C(24) –H(24)…N(4) [x,y,z]	0.93	2.57	3.105(10)	117
	C(44) –H(44)…N(5) [x,y,z]	0.93	2.29	2.897 (10)	122
	C(45) –H(45)…S(1) [1+x,y,z]	0.98	2.82	3.777 (11)	166
Complex 3	N(3) –H(3)...Cl(1) [x,y,z]	0.86	2.51	2.939(3)	122
	N(6) –H(6)...Cl(3) [x,y,z]	0.86	2.53	2.941(3)	110
	C(2) –H(2)...N1(4) [x,y,z]	0.93	2.58	3.107 (5)	116
	C(22) –H(22)...N(2) [x,y,z]	0.93	2.31	2.879 (5)	119
	C(34) –H(34)...N(4) [x,y,z]	0.93	2.58	3.159 (4)	121
	C(37)–H(37)...S(2)[x,1/2-y,-1/2+z]	0.93	2.82	3.753 (3)	177
	C(44) –H(44)...N(5) [x,y,z]	0.93	2.31	2.856 (4)	117