Syntheses, Crystal Structures, and Optical Properties of Five Metal Complexes Constructed from a V-shaped Thiophene-containing Ligand and Different Dicarboxylate Ligands

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Table S1. Selected Bond Lengths (Å) and Angles (deg) for complexes **1-5**.

Complex **1**			
Ni(1)-O(1)	2.0202(15)	Ni(1)-O(5)	2.0859(16)
N(1)-Ni(1)	2.058(2)	Ni(1)-O(3)#1	2.1532(15)
Ni(1)-O(4)#1	2.1415(17)	Ni(1)-N(3)#2	2.060(2)
O(1)-Ni(1)-N(1)	90.69(8)	O(1)-Ni(1)-O(5)	98.84(7)
N(1)-Ni(1)-O(5)	87.75(8)	O(1)-Ni(1)-O(4)#1	98.86(6)
N(1)-Ni(1)-O(4)#1	91.45(8)	O(1)-Ni(1)-O(3)#1	160.47(7)
O(5)-Ni(1)-O(4)#1	162.29(6)	N(1)-Ni(1)-O(3)#1	89.76(7)
O(5)-Ni(1)-O(3)#1	100.69(6)	O(1)-Ni(1)-N(3)#2	90.02(7)
N(1)-Ni(1)-N(3)#1	177.35(8)	N(3)#2-Ni(1)-O(5)	89.62(7)

N(3)#2-Ni(1)-O(4)#1	90.95(8)	N(3)#2-Ni(1)-O(3)#1	90.42(7)
O(4)#2-Ni(1)-O(3)#1	61.61(6)		
Symmetry codes: #1 = -1+*x*, *y*, *z*; #2 = -*x*, 2-*y*, -*z*.			
Complex **2**			
Zn(1)-O(1)	1.962(5)	Zn(1)-N(1)	1.990(5)
Zn(1)-O(3)#1	1.936(5)	Zn(1)-N(3)#2	2.022(7)
O(1)-Zn(1)-N(1)	119.4(2)	O(3)#1-Zn(1)-O(1)	105.6(2)
O(3)#1-Zn(1)-N(1)	111.5(2)	O(3)#1-Zn(1)-N(3)#2	115.3(2)
O(1)-Zn(1)-N(3)#2	98.6(3)	N(1)-Zn(1)-N(3)#2	106.2(2)
Symmetry codes: #1 = *x*, *y*, 1+*z*; #2 = *x*, -1+*y*, *z*.			
Complex **3**			
Zn(1)-O(2)	1.957(2)	Zn(1)-N(1)	1.994(3)
Zn(1)-O(3)#1	1.948(2)	Zn(1)-N(3)#2	2.037(2)
O(2)-Zn(1)-N(1)	119.50(11)	O(3)#1-Zn(1)-O(2)	102.99(11)
O(3)#1-Zn(1)-N(1)	127.16(11)	O(2)-Zn(1)-N(3)#2	101.05(10)
N(1)-Zn(1)-N(3)#2	98.91(10)	O(3)#1-Zn(1)-N(3)#2	102.37(11)
Symmetry codes: #1 = *x*, -*y*, -0.5+*z*; #2 = 0.5-*x*, 0.5-*y*, 1-*z*.			
Complex **4**			
Co(1)-O(1)	1.9432(16)	Co(1)-N(1)	2.0390(18)
Co(1)-N(4)#1	2.0212(18)	Co(1)-O(3)#2	1.9479(16)
O(1)-Co(1)-N(1)	116.49(7)	O(1)-Co(1)-N(4)#1	112.18(8)
N(4)#1-Co(1)-N(1)	103.55(7)	O(1)-Co(1)-O(3)#2	107.20(7)
O(3)#2-Co(1)-N(1)	99.92(7)	O(3)#2-Co(1)-N(4)#1	117.27(7)
Symmetry codes: #1 = *x*, 0.5-*y*, -0.5+*z*; #2 = 3-*x*, 0.5+*y*, 0.5-*z*.			
Complex **5**			
Co(1)-O(1)	2.0592(13)	Co(1)-O(2)#2	2.0140(14)

Co(1)-O(3)#3	2.1216(14)	Co(1)-O(4)#4	2.0196(14)
Co(1)-N(1)	2.0539(15)		
N(1)-Co(1)-O(1)	93.65(6)	O(2)#2-Co(1)-N(1)	104.07(6)
O(2)#2-Co(1)-O(1)	161.57(6)	O(2)#2-Co(1)-O(3)#3	87.78(6)
N(1)-Co(1)-O(3)#3	92.91(6)	O(1)-Co(1)-O(3)#3	86.30(6)
O(4)#4-Co(1)-O(1)	87.42(6)	O(2)#2-Co(1)-O(4)#4	92.86(6)
O(4)#4-Co(1)-N(1)	104.62(7)	O(4)#4-Co(1)-O(3)#3	161.72(7)
Symmetry codes: #2: 1-*x*, 1-*y*, 1-*z*; #3: *x*, -*y*, -0.5+*z*; #4: 1-*x*, 1+*y*, 1.5-*z*.			

Synthesis of 2,8-di(1*H*-imidazol-1-yl)dibenzothiophene (DIDP)

A mixture of 2,8-dibromodibenzo[*b*,*d*]thiophene (3.42g, 10 mmol), imidazole (13.62g, 200 mmol), anhydrous potassium carbonate (27.64 g, 200 mmol), anhydrous $CuSO_4$ (0.16g, 1 mol) in dry DMF (20 mL) was heated to 150 °C for 3 days under argon atmosphere. The mixture was then cooled to room temperature. Solvent was removed by distillation under a vacuum. Then the resulting residue was dissolved in $CHCl_3$ (200 mL) and washed thoroughly by water to remove excess imidazole. The organic layer was dried by anhydrous $MgSO_4$ and filtered. Then the desired compound DIDP was separated by silica gel column chromatography (EA/CH_3OH = 2:1) to afford off-white powder in a yield 1.90 g (60%). ^{1}H NMR(500 MHz, DMSO): δ: 8.83 (s, 2H), 8.40 (d, 2H), 8.23 (d, 2H), 7.89 (d, 4H), 7.21 (s, 2H). EI-TOF-MS (*m*/*z*): calcd for $[C_{18}H_{12}N_4S]^+$ 316.4, found 316.2. IR(KBr, cm^{-1}): 3437(w), 3106(w), 1630(m), 1604(m), 1563(w), 1499(vs), 1445(w), 1309(w), 1251(m), 1053(s), 660(m). Anal. calcd for $C_{18}H_{12}N_4S$: C, 68.33%; H, 3.82%; N, 17.71%. Found: C, 68.23%; H, 3.88%; N, 17.79%.

Table S2. Hydrogen bond lengths (Å) and angles (º) for the complexes **1** and **4**

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA	Symmetry code
Complex **1**					
O(5)–H(5B)···O(2)	0.85	2.05	2.678(2)	130.6	*x*, *y*, *z*

O(5)–H(5C)···S(1)	0.85	2.78	3.4751(2)	139.6	*-x*, 1-*y*, *-z*
Complex **4**					
C(24)–H(24)···O(4)	0.93	2.28	3.203(3)	169.2	-1+*x*, *y*, *z*

Table S3. Luminescence data for organic ligands and complexes in the solid state.

	λ_{ex}[nm]	λ_{em}[nm]
2	295	418
3	303	445
DIDP	383	435
H_2hfipbb	290	325
4,4'-H_2sdb	296	344

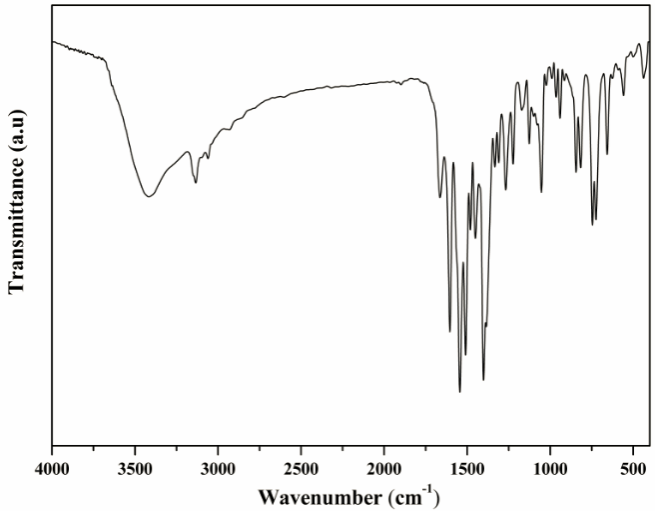


Figure S1. IR spectra of complex **1**

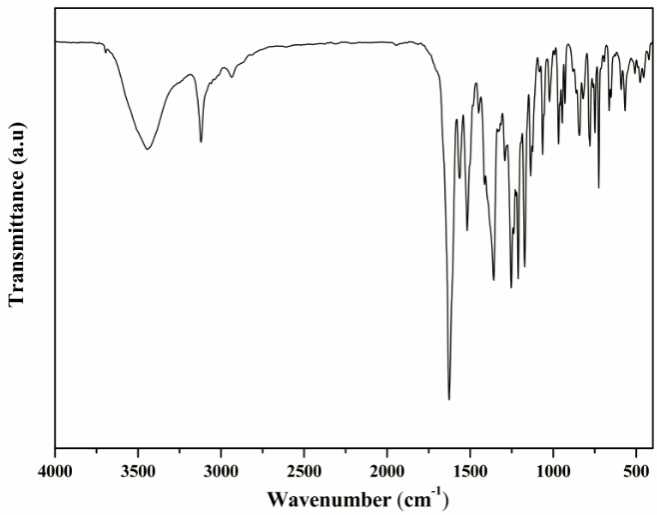


Figure S2. IR spectra of complex 2

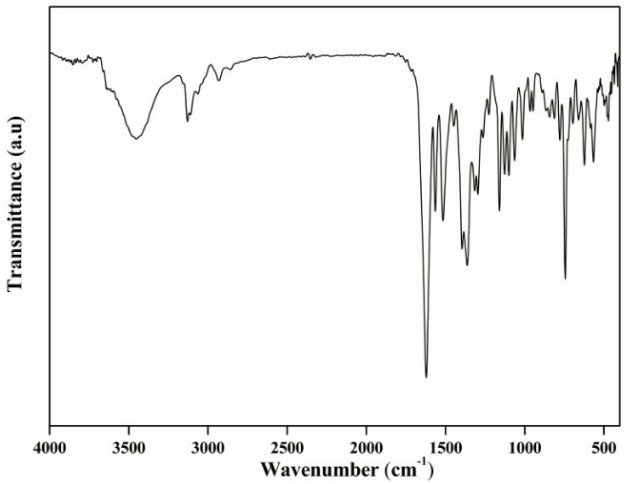


Figure S3. IR spectra of complex **3**

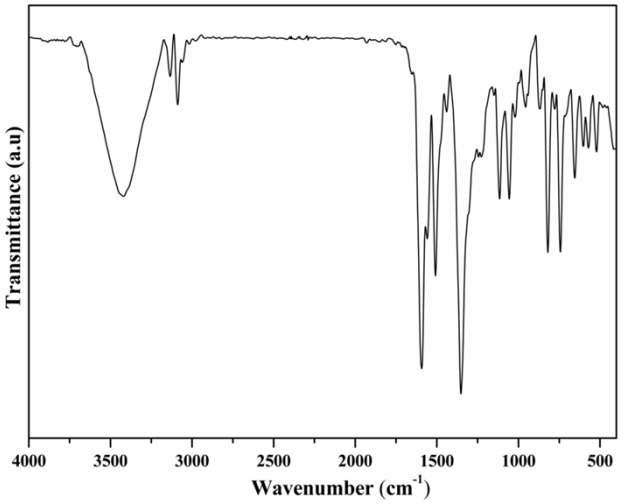


Figure S4. IR spectra of complex **4**

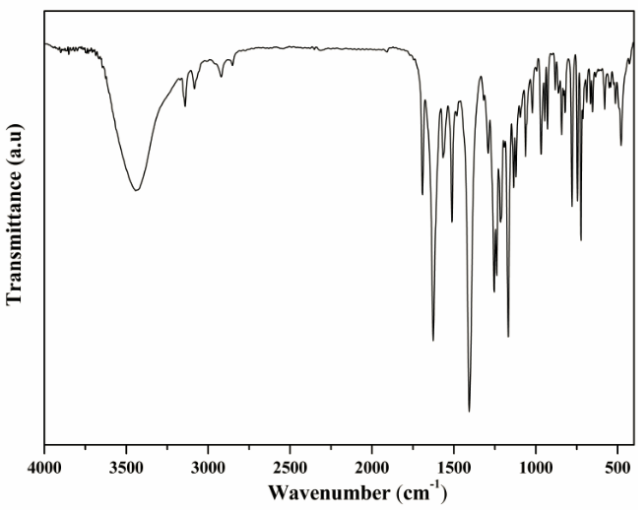
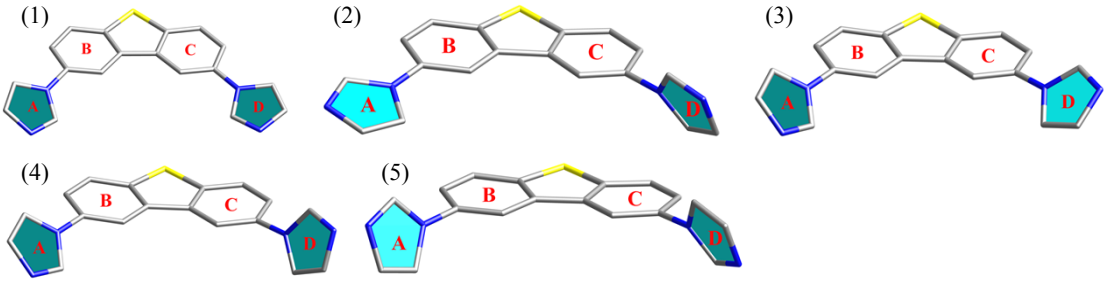


Figure S5. IR spectra of complex **5**



Scheme 2. Schematic Representations of the Coordination modes of Im Section of DIDP in complexes **1**−**5**

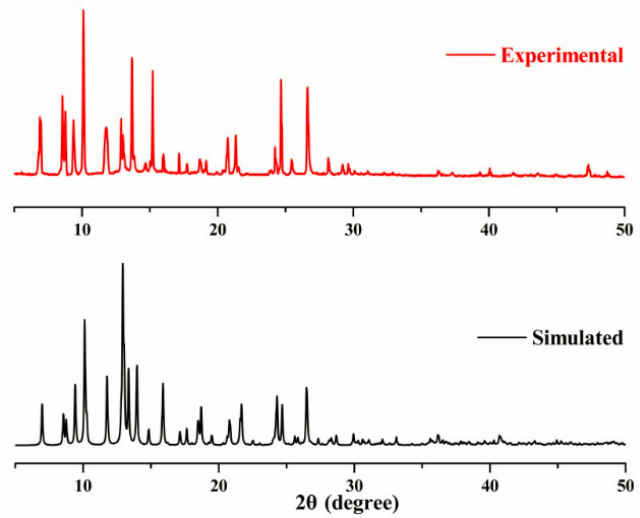


Figure S6. Powder X-ray diffraction patterns of complex **1**

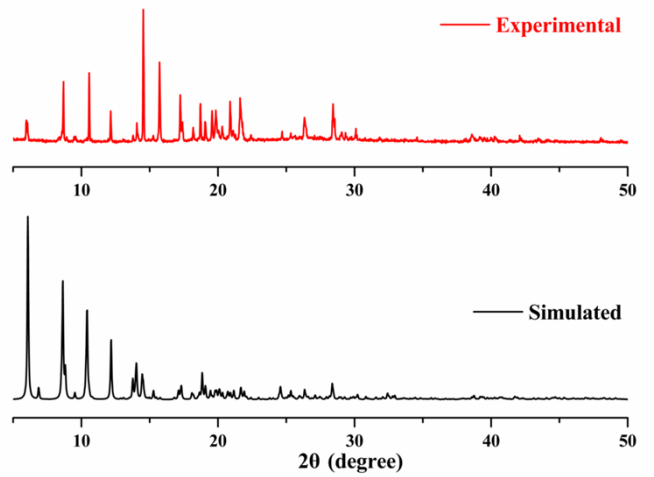


Figure S7. Powder X-ray diffraction patterns of complex **2**

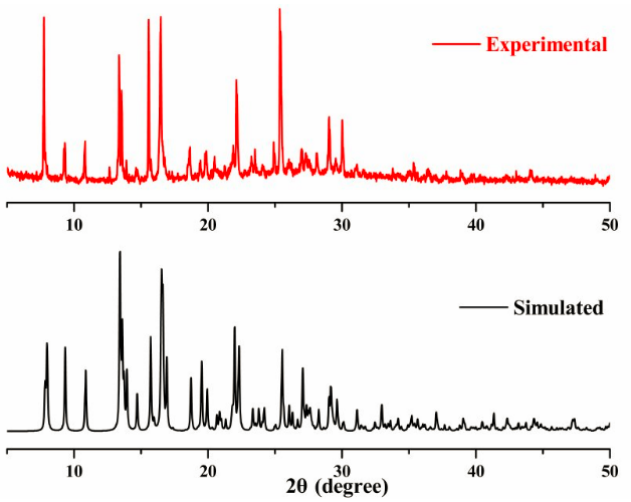


Figure S8. Powder X-ray diffraction patterns of complex **3**

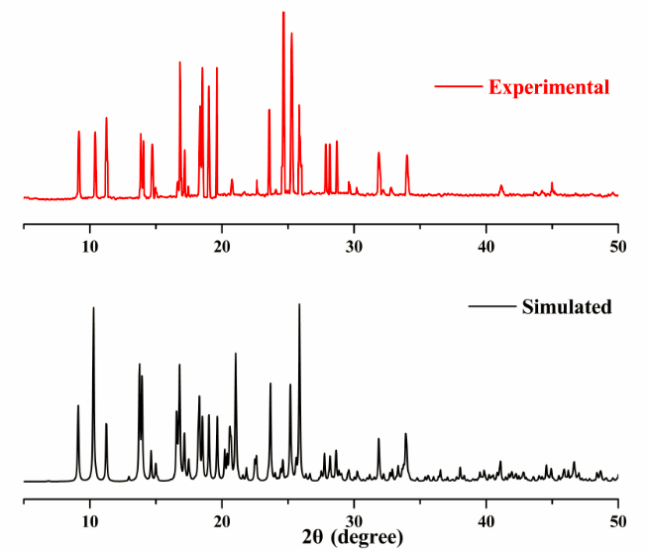


Figure S9. Powder X-ray diffraction patterns of complex **4**

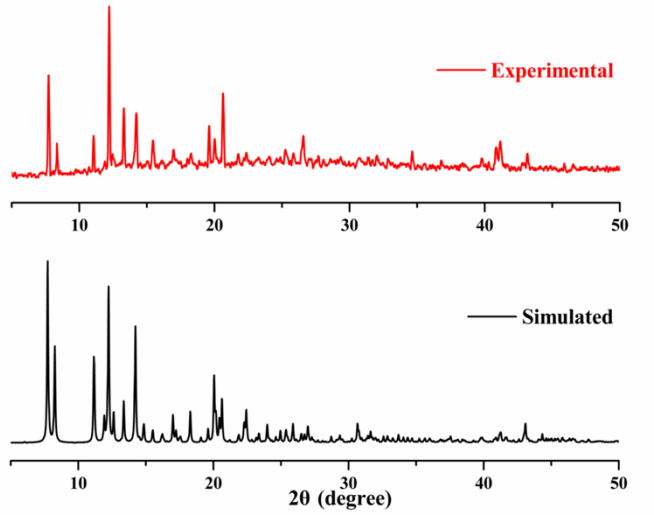


Figure S10. Powder X-ray diffraction patterns of complex **5**

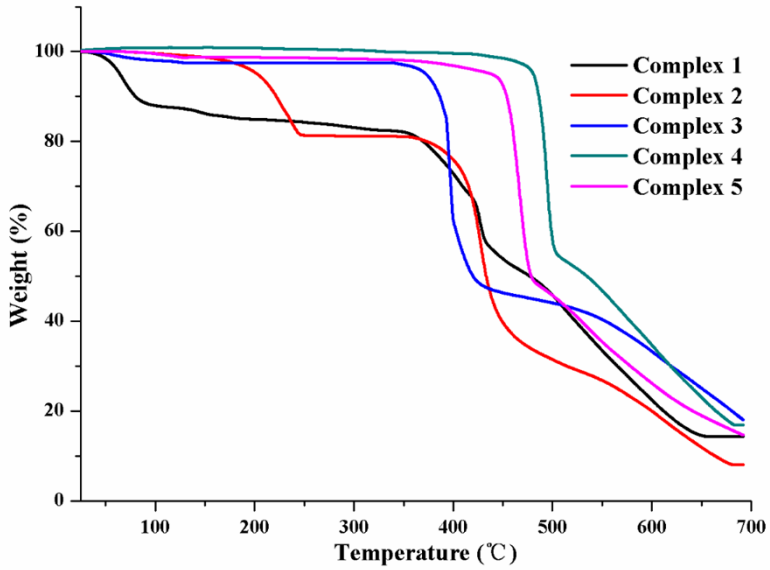


Figure S11. TGA curves of complexes **1-5**

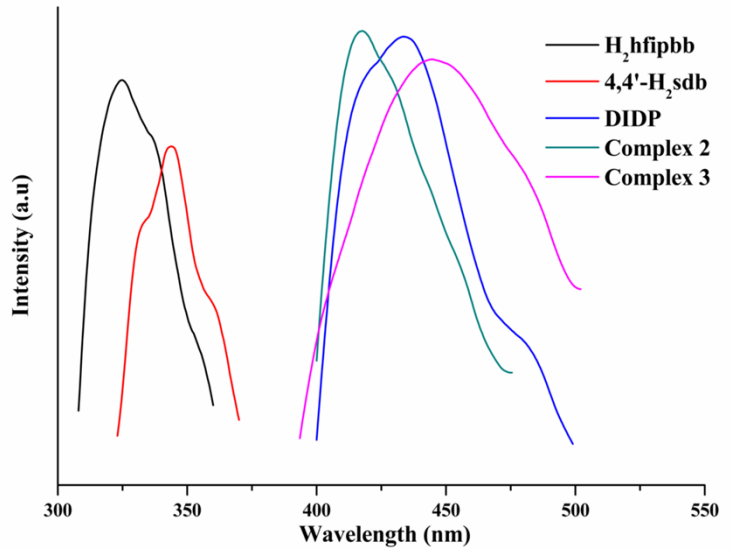
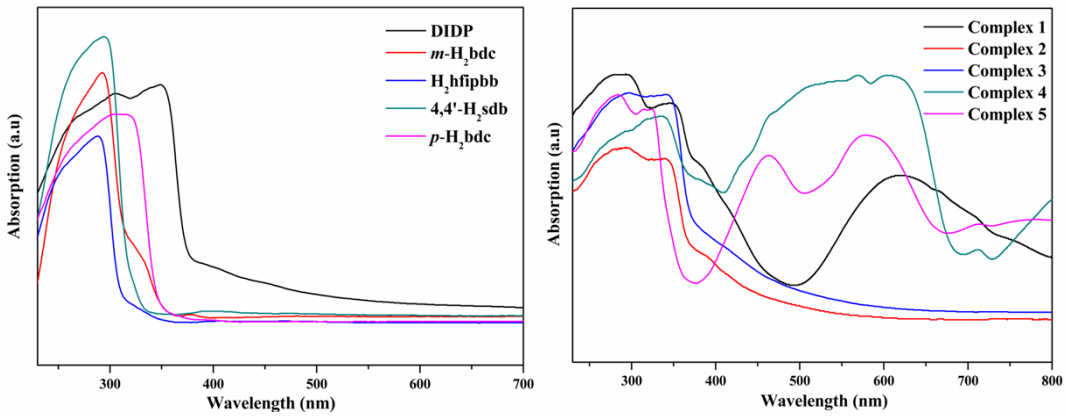


Figure S12. Solid-state photoluminescent spectra of **2**, **3** and corresponding ligands at room temperature

(a)



(b)

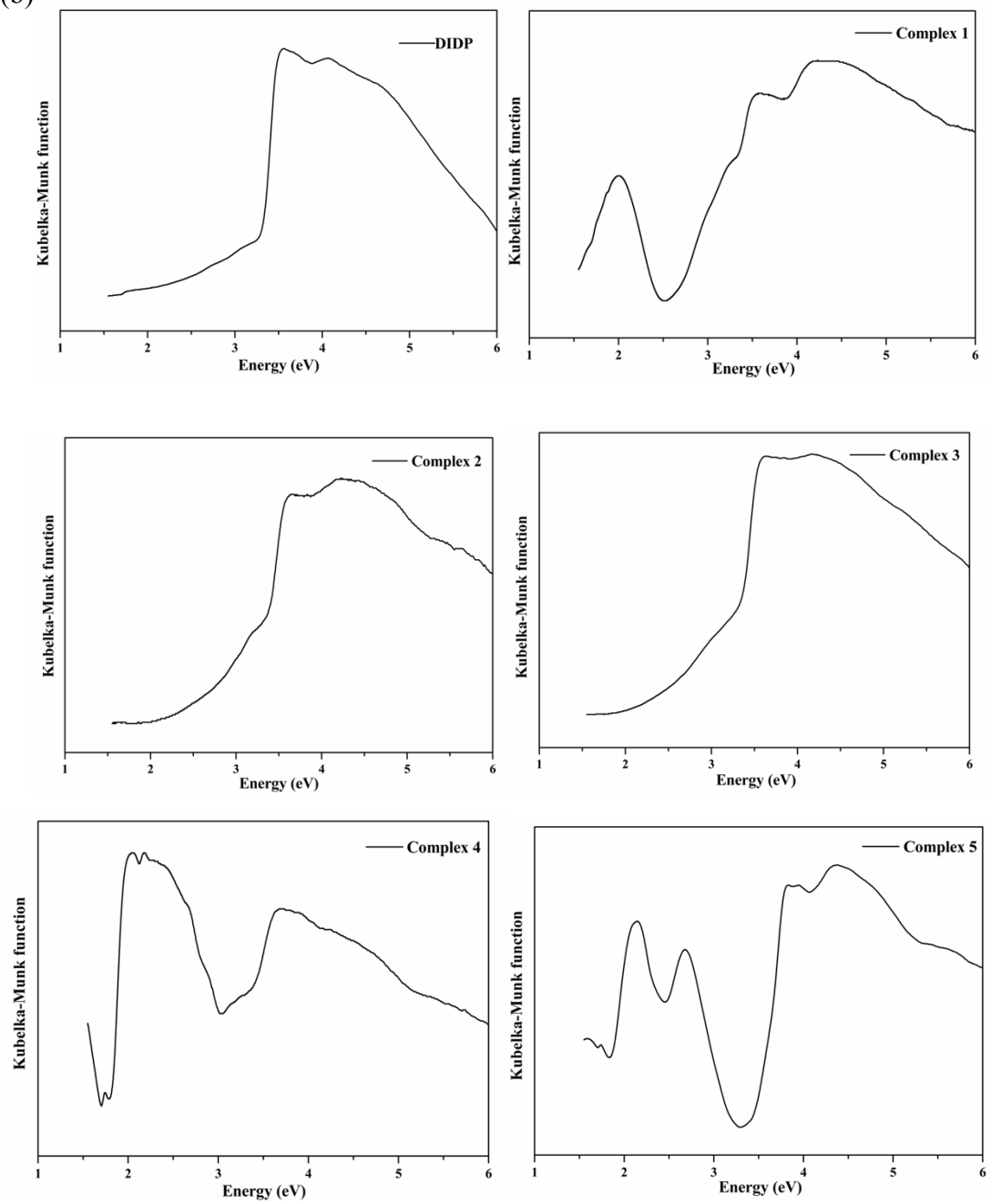


Figure S13. (a) UV-vis absorbance spectra and (b) Plot of Kubelka-Munk as a function of energy of the complexes and the free ligands at room temperature