Dinuclear copper(II) complexes based on two multidentate flexible Schiff-base ligands and one unusual *in situ* formed diphenolate 2,6-piperidin-4-one derivative

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Electronic Supporting Information

Syntheses of Schiff-base ligands HL_1 and HL_2.

HL_1: *N*-(3-Aminopropyl)imidazole (2.05 g, 16.4 mmol) was added into an ethanol solution (20 cm^3) of 3,5-dichlorosalicylaldehyde (3.13 g, 16.4 mmol), and three drops of glacial acetic acid were added. The mixture was refluxed for 5 h and cooled to room temperature. The solvent was removed by a rotatory evaporator and the yellow solid HL_1 was obtained in a yield of 3.81 g (78 %). M.P: 90–92 ℃. *Anal.* Calc. for $C_{13}H_{13}Cl_2N_3O$: C, 52.37; H, 4.39; N, 14.09 %. Found: C, 52.25; H, 4.12; N, 13.95 %. Main FT–IR absorptions (KBr pellets, cm^{-1}): 3438 (w), 1637 (vs), 1508 (m), 1450 (s), 1222 (m), 748 (m). ^{1}H NMR (300 MHz, CD_3OD) δ = 8.40 (s, 1H, H_c), 7.72 (s, 1H, H_g), 7.45 (d, J = 1.8 Hz, 1H, H_h), 7.28 (d, J = 1.8 Hz, 1H, H_i), 7.19 (s, 1H, H_a), 6.98 (s, 1H, H_b), 4.17 (t, J = 6.9 Hz, 2H, H_f), 3.66 (t, J = 6.8 Hz, 2H, H_d), 2.20-2.29 (tt, J = 6.6 and 6.9 Hz, 2H, H_e). ^{13}C NMR (75 MHz, CDCl3): δ = 163.8, 156.3, 131.1, 128.3, 121.6, 121.0, 118.6, 53.7, 43.4, 30.5 ppm. UV–Vis in methanol, λ_{max} = 372 and 295 nm. ESI–TOF–MS (negative): m/z = 296.25 (100 %), $[M-H]^-$.

HL_2: Synthesis of HL_2 was similar to that of HL_1 except that 3,5-dibromosalicylaldehyde (6.35 g, 16.4 mmol) was used. Yield: 5.33 g (84 %). M.P: 105–107 ℃ *Anal.* Calc. for $C_{13}H_{13}Br_2N_3O$: C, 40.34; H, 3.39; N, 10.86 %. Found: C, 40.18; H, 3.56; N, 10.77 %. Main FT–IR absorptions (KBr pellets, cm^{-1}): 3415 (w), 3051(w), 1638 (vs), 1501 (s), 1448 (s), 1228 (m), 865 (m). ^1H NMR (300 MHz, CD_3OD) δ = 8.38 (s, 1H, H_c), 7.74 (d, J = 2.4 Hz, 1H, H_h), 7.69 (s, 1H, H_g), 7.48 (d, J = 2.4 Hz, 1H, H_i), 7.18 (s, 1H, H_a), 6.97 (s, 1H, H_b), 4.17 (t, J = 7.1 Hz, 2H, H_f), 3.66 (t, J = 6.8 Hz, 2H, H_d), 2.20-2.29 (tt, J = 6.9 and 6.9 Hz, 2H, H_e). ^{13}C NMR (75 MHz, CD3OD): δ = 166.6, 163.4, 139.6, 135.0, 119.9, 115.3, 108.1, 53.9, 45.5, 32.5 ppm. UV–Vis in methanol, λ_{max} = 375 and 291 nm. ESI–TOF–MS (negative): m/z = 385.83 (100 %), $[M-H]^-$.

Table SI1 Selected bond angles (°) for **1, 2** and **3**.

1			
O2–Cu1–O1	161.5(1),	O2–Cu1–N1	88.6(1)
O1–Cu1–N1	90.8(1),	O2–Cu1–N4	90.7(1)
O1–Cu1–N4	88.8(1)	N1–Cu1–N4	176.6(1)
O2–Cu1–N3A	96.6(1)	O1–Cu1–N3A	101.8(1),
N1–Cu1–N3A	94.4(1),	N4–Cu1–N3A	89.2(1)
2			
O1–Cu1–O2	162.0(5)	O1–Cu1–N4	87.4(6),
O2–Cu1–N4	90.5(5),	O1–Cu1–N1	92.0(6),
O2–Cu1–N1	89.0(5),	N4–Cu1–N1	176.2(6)
O1–Cu1–N3A	100.9(6)	O2–Cu1–N3A	97.0(5)
N4–Cu1–N3A	88.9(6)	N1–Cu1–N3A	94.9(6)
3			
O1–Cu1–O3	171.4(2)	O1–Cu1–N1	86.9(2)
O3–Cu1–N1	88.2(2),	O1–Cu1–N3	92.4(2)
O3–Cu1–N3	93.8(2)	N1–Cu1–N3	168.6(2)

Table SI2. Hydrogen bonding parameters (Å, °) in complex **3**.

D–H···A	*d* (D–H)	*d* (H···A)	*d* (D···A)	∠DHA	Sym. Code
3					
O7–H7B···O3	0.85	2.30	2.890(1)	127	1-*x*, 1-*y*, 2-*z*
C15–H15···Cl2	0.93	2.66	3.547(6)	160	
C21–H21A···O1	0.97	2.60	3.190(7)	119	

C22–H22B··· O3	0.97	2.54	3.149(8)	121

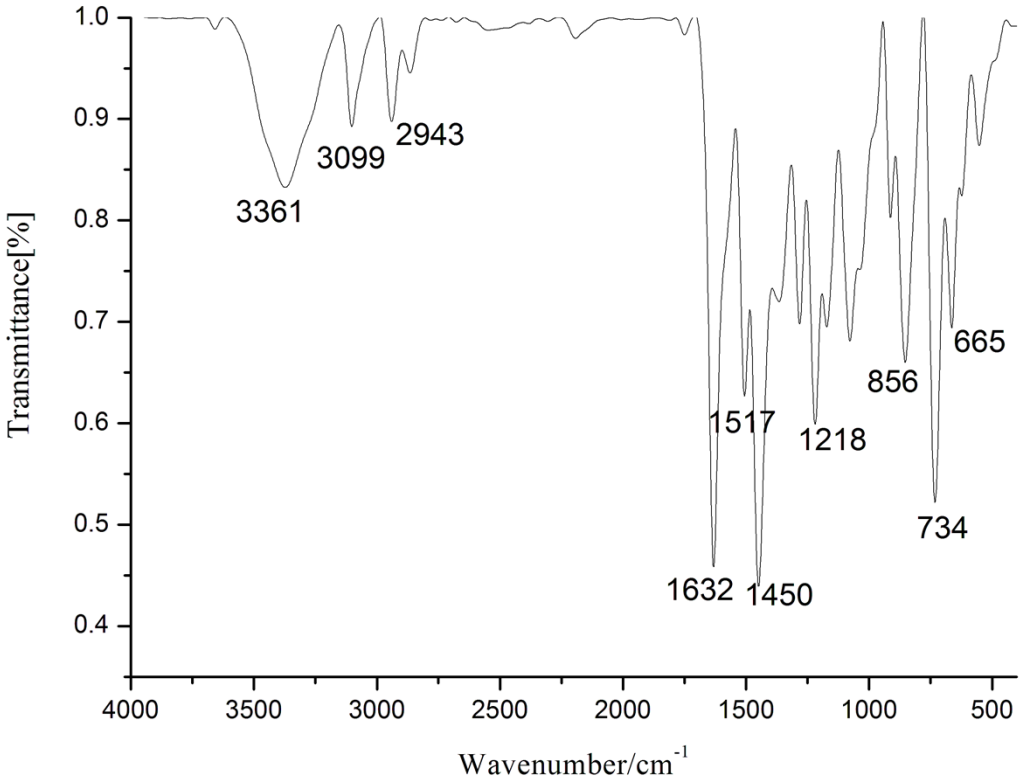

Fig. SI1 FT–IR spectrum of ligand HL_1.

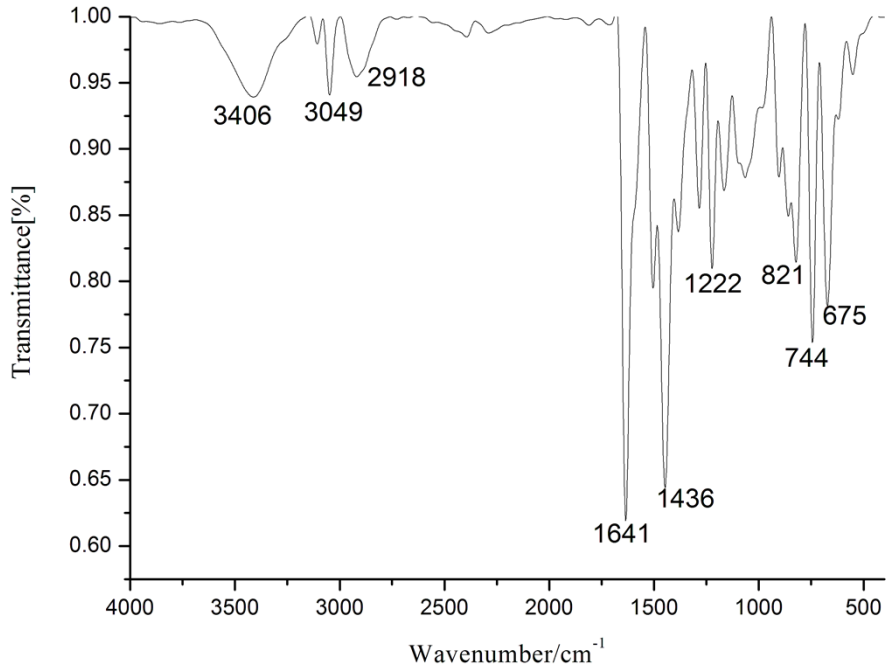

Fig. SI2 FT–IR spectrum of ligand HL_2.

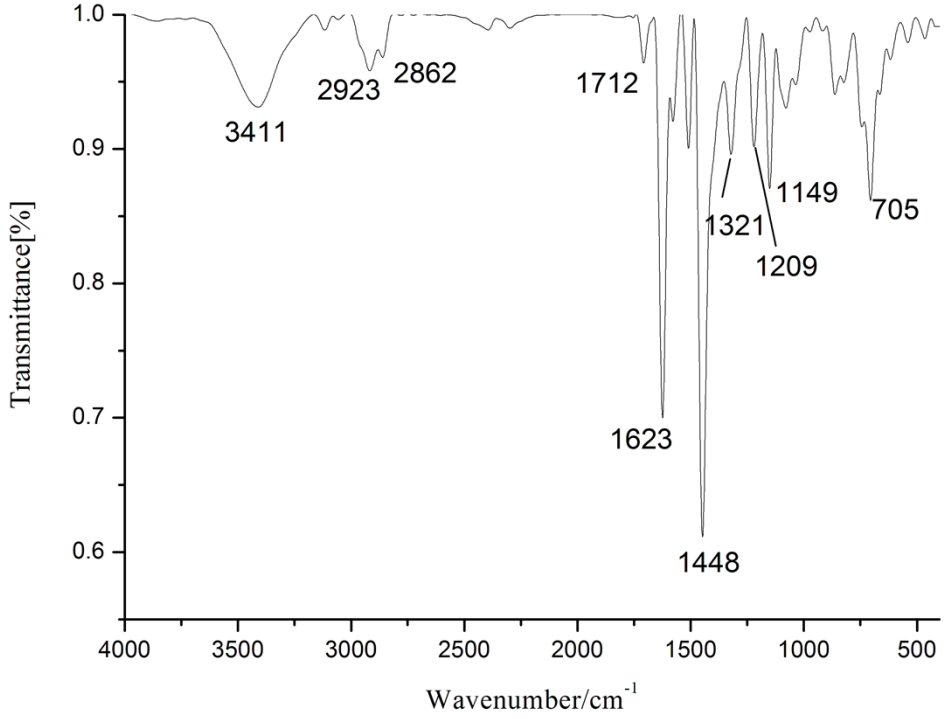

Fig. SI3 FT–IR spectrum of complex **1**.

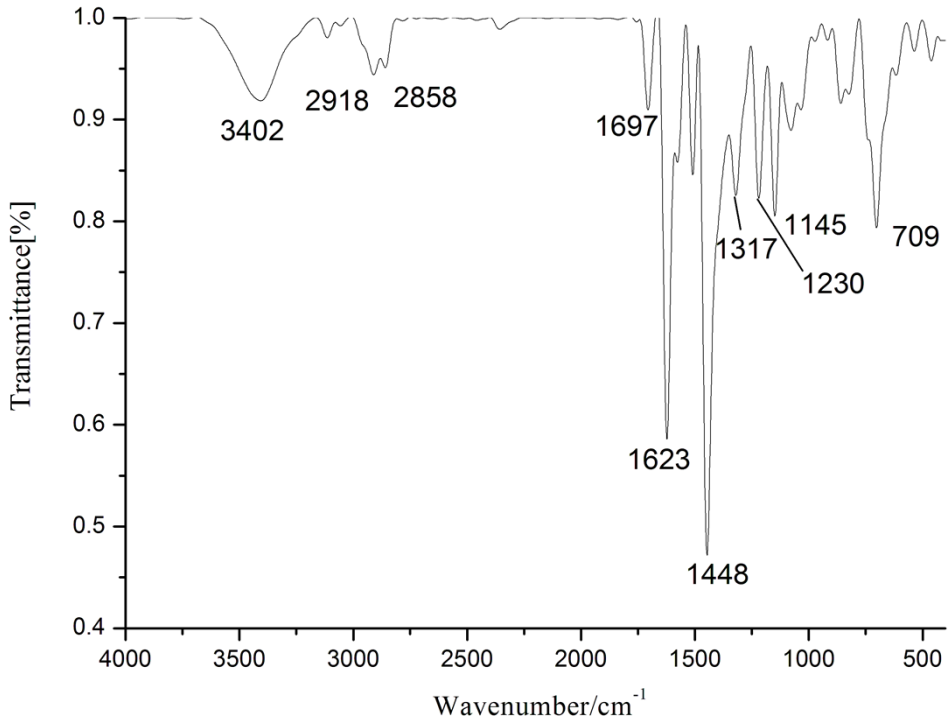

Fig. SI4 FT–IR spectrum of complex **2**.

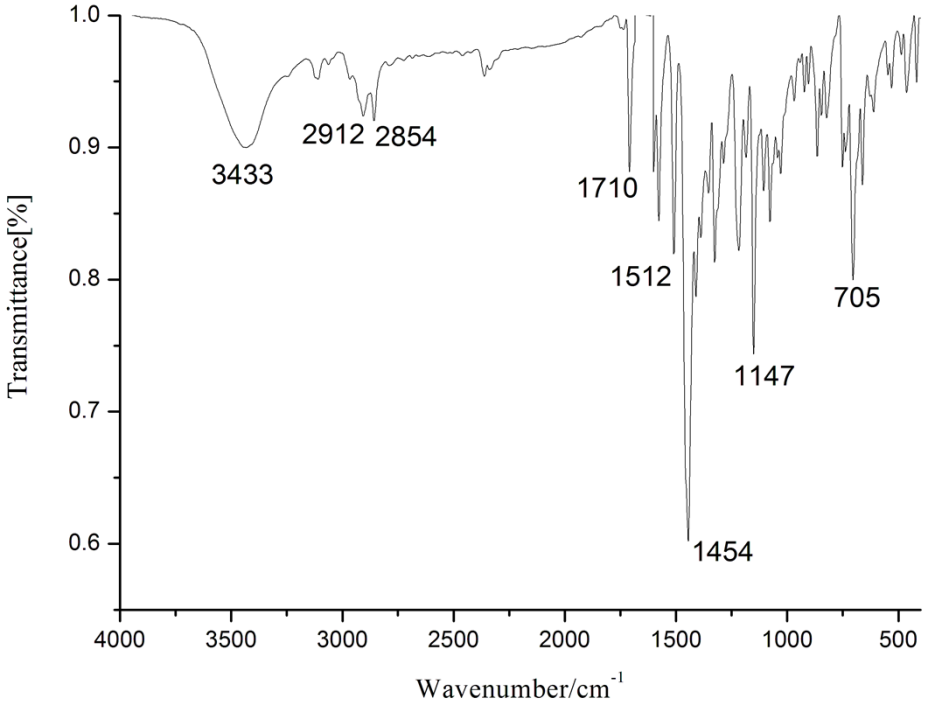

Fig. SI5 FT–IR spectrum of complex **3**.

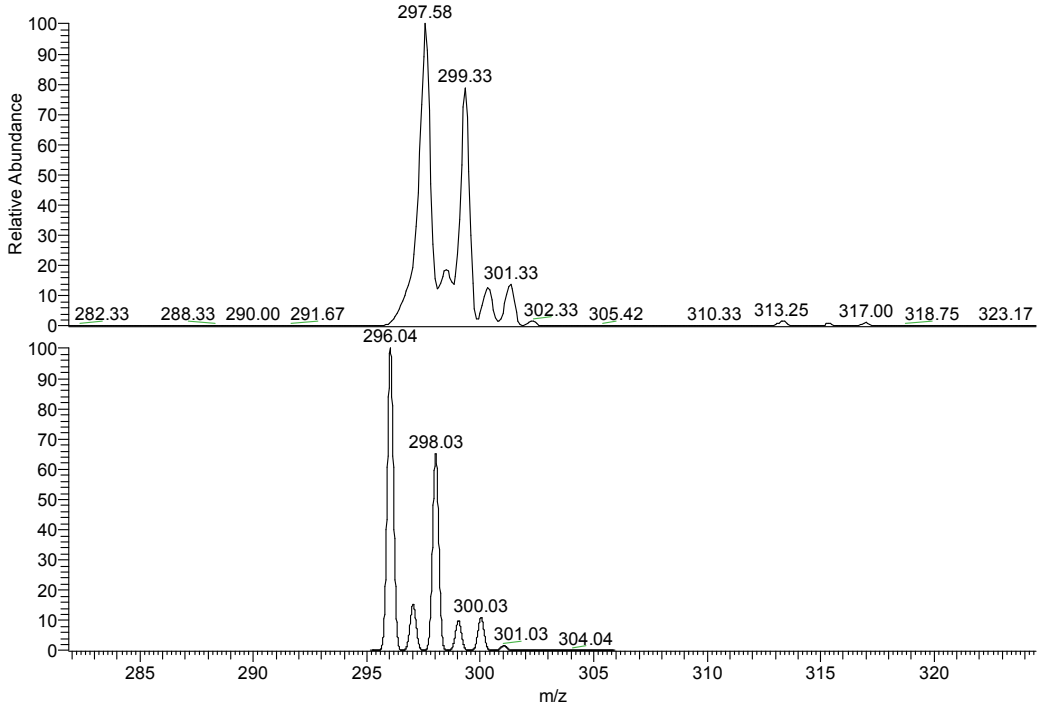

Fig. SI6 Negative ESI–MS (top) and simulated one with isotope distribution (bottom) for ligand HL_1.

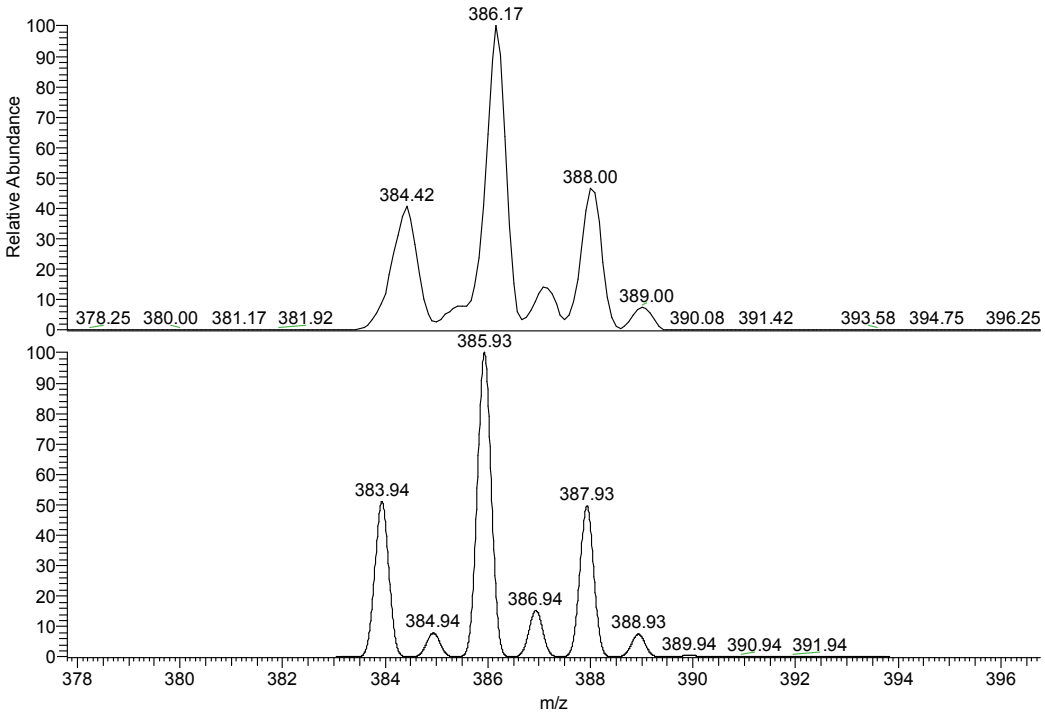

Fig. SI7 Negative ESI–MS (top) and simulated one with isotope distribution (bottom) for ligand HL_2.

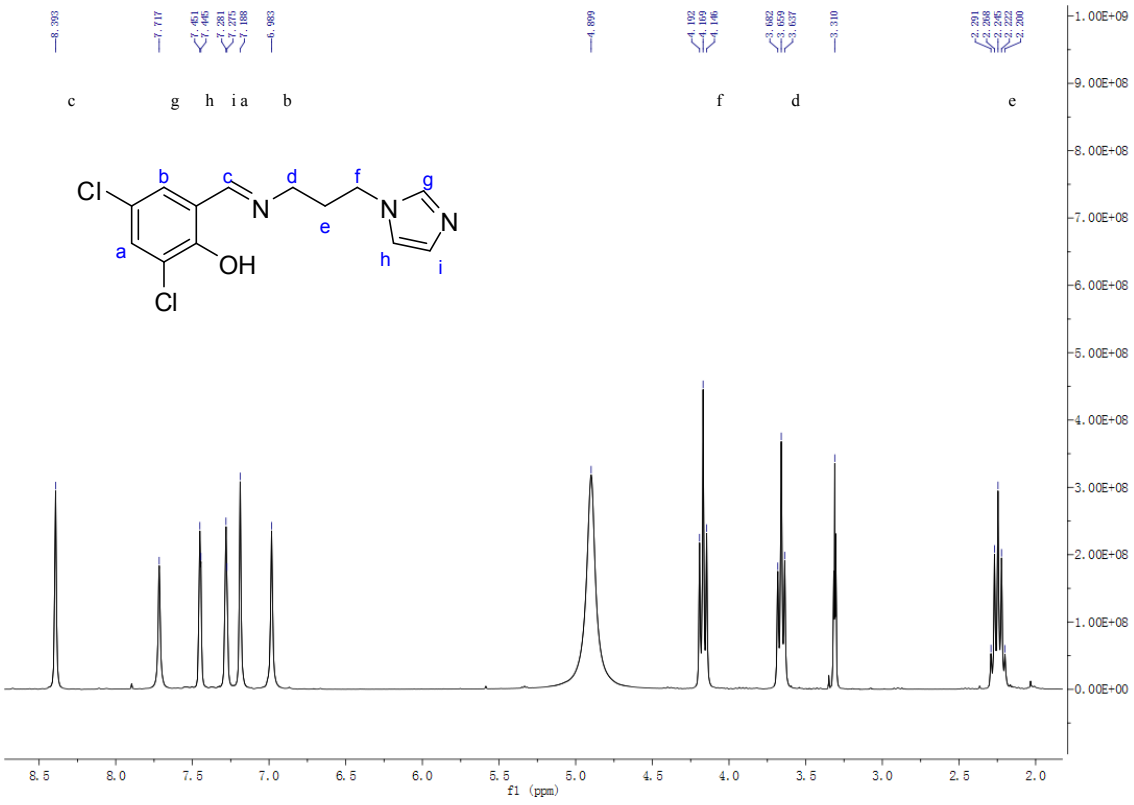

Fig. SI8 ^{1}H NMR spectrum of HL_1.

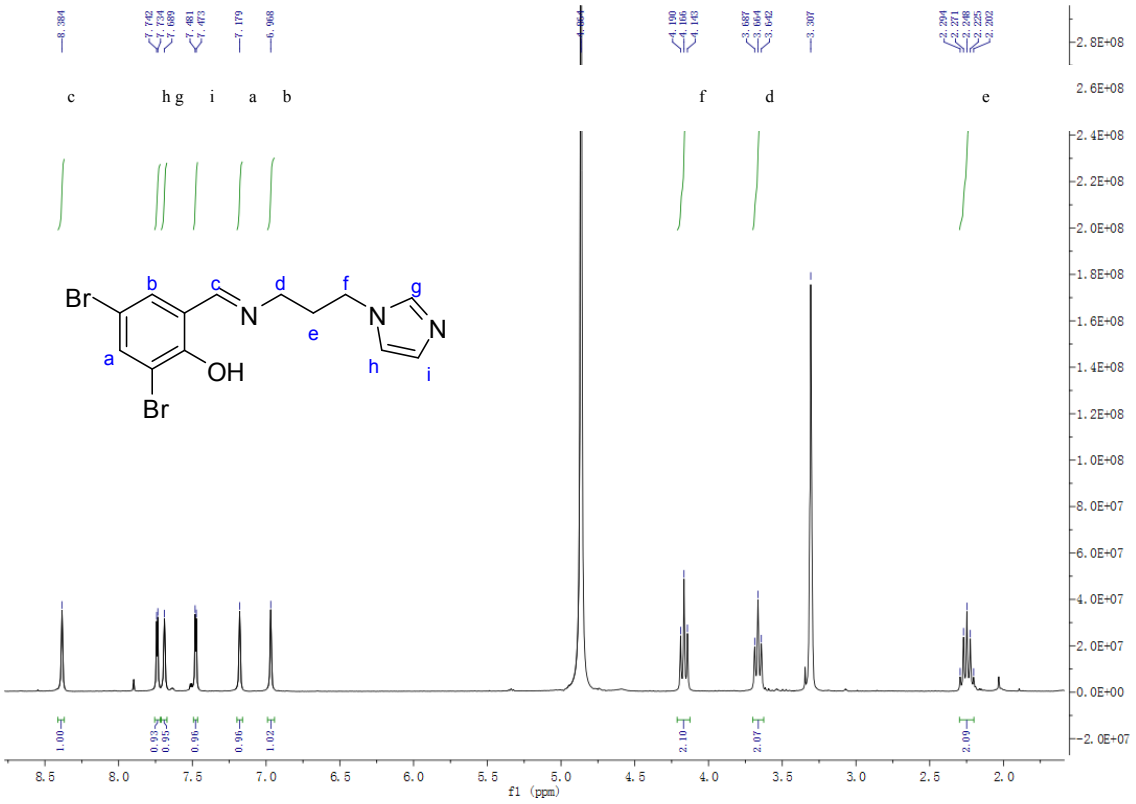

Fig. SI9 ^{1}H NMR spectrum of HL_2.

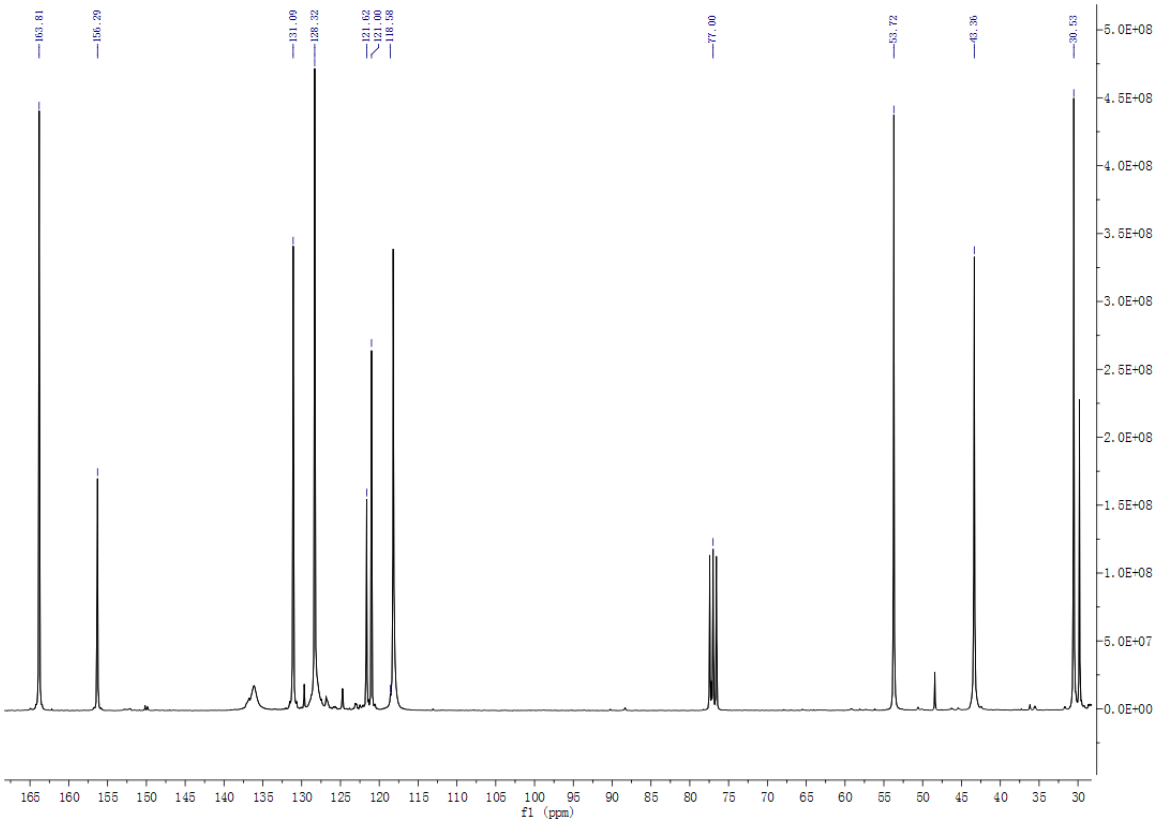

Fig. SI10 ^{13}C NMR spectrum of HL_1.

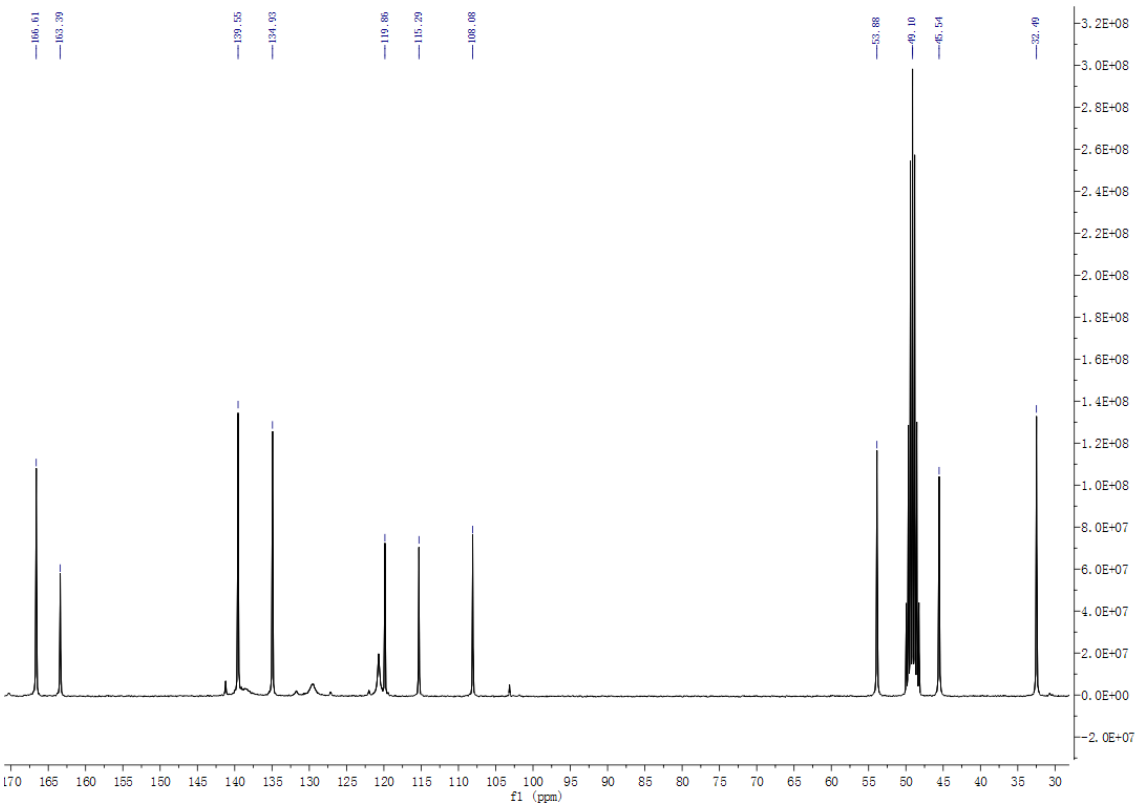

Fig. SI11 ^{13}C NMR spectrum of HL_2.

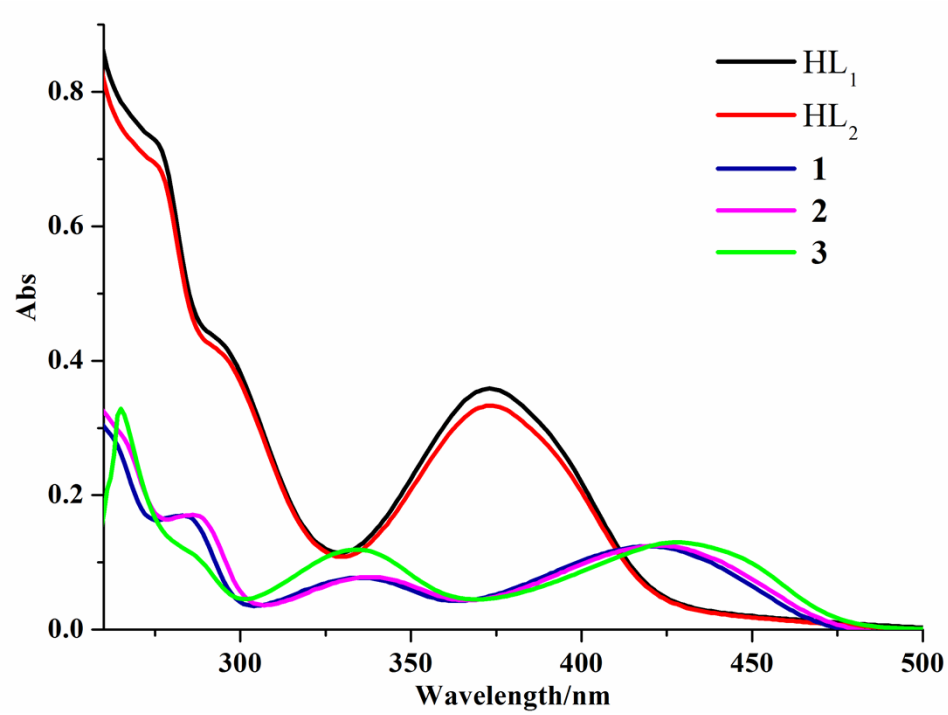

Fig. SI12 UV-Vis spectral comparisons for HL_1, HL_2, complexes **1** and **2** in methanol as well as complex **3** in DMF.

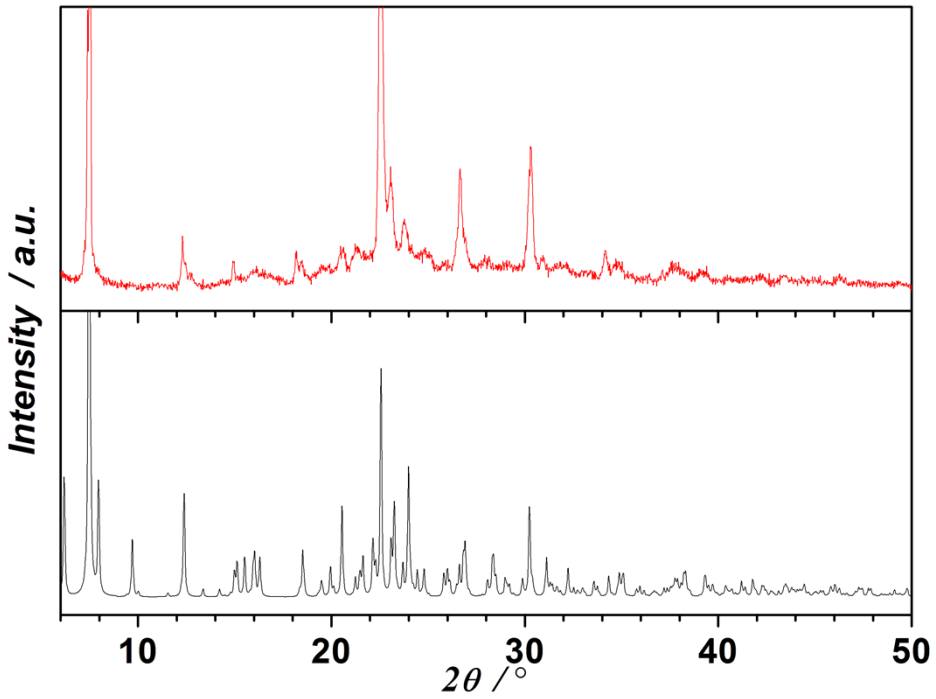

Fig. SI13 The simulative (black line) and experimental (red line) powder X-ray diffraction patterns for complex **1**.

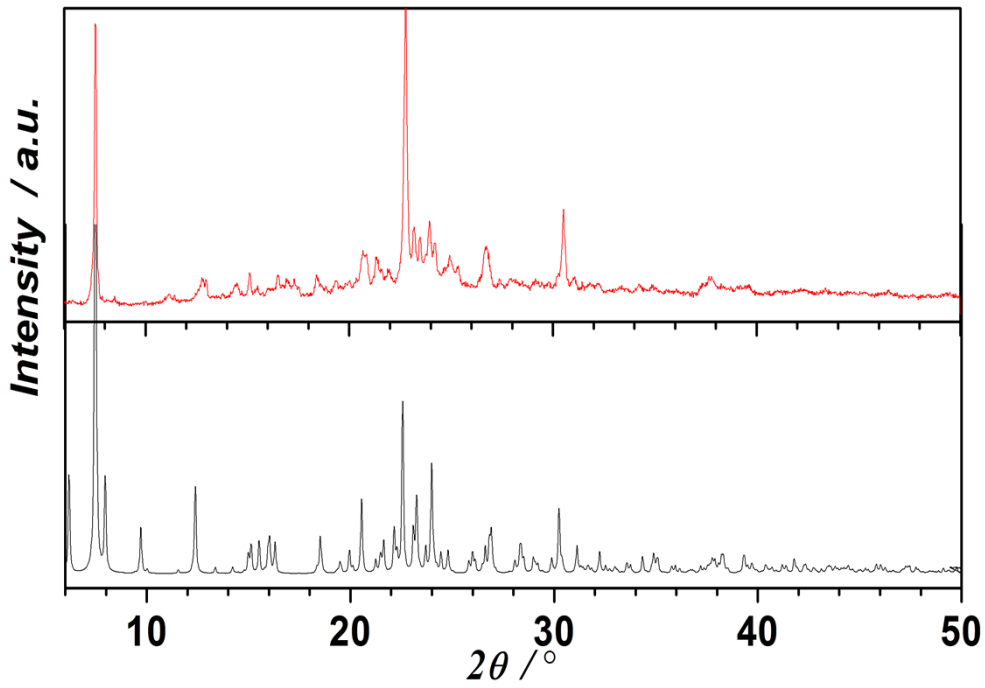

Fig. SI14 The simulative (black line) and experimental (red line) powder X-ray diffraction patterns for complex **2**.

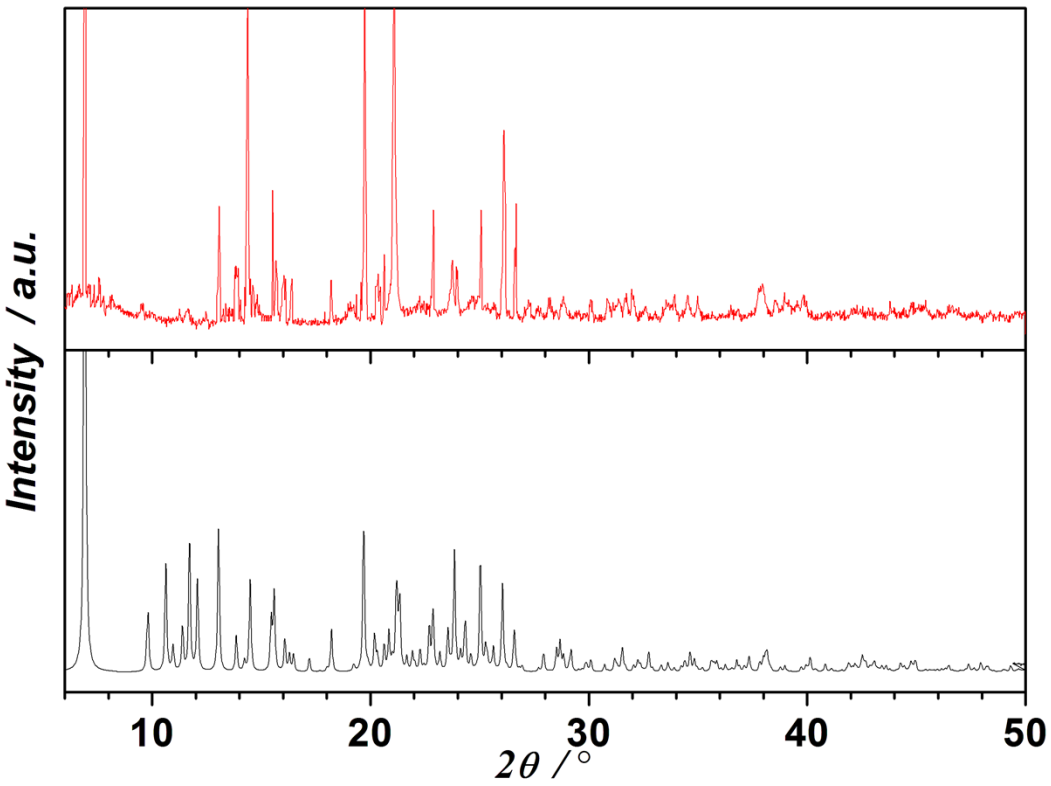

Fig. SI15 The simulative (black line) and experimental (red line) powder X-ray diffraction patterns for complex **3**.

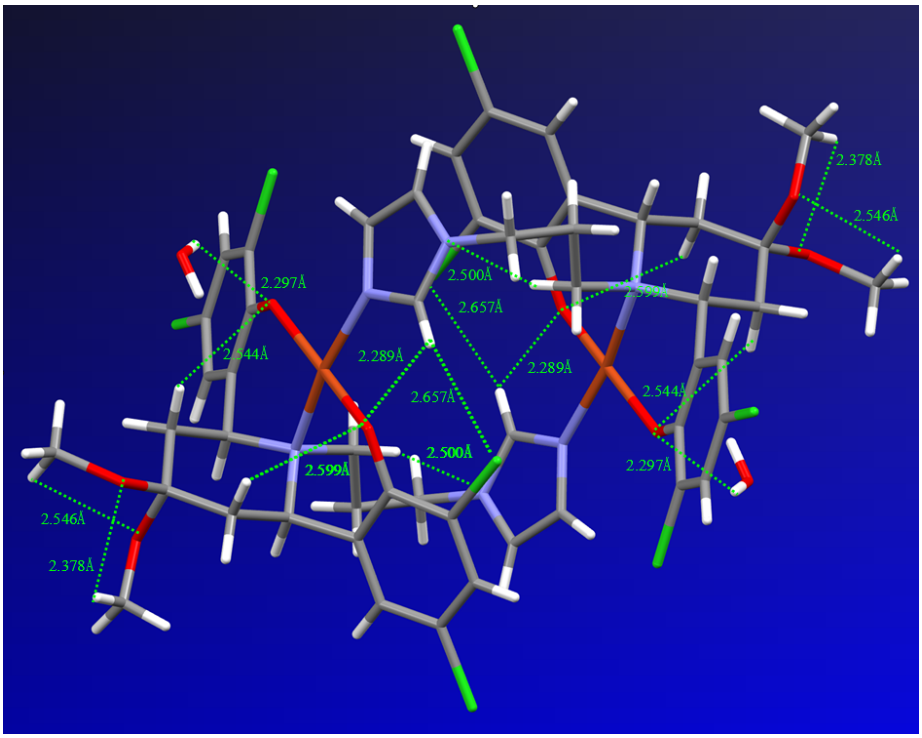

Fig. SI16 Perspective view of the hydrogen bonding interactions in complex **3**.