Supporting Information for

Role of anions in preparing silver(I) complexes with a new multidentate ligand: polymorphs, structures and nolinear optical propreties

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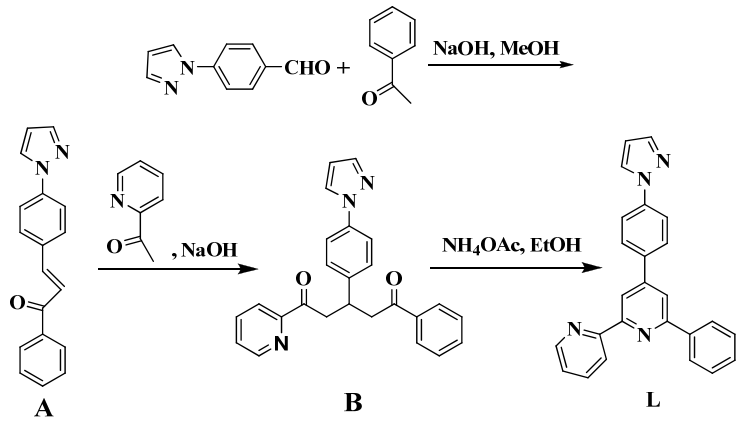

Scheme S1 Synthetic route to **L**

Experimental section

Synthesis of A

A methanol solution (40 mL) of NaOH (4.00 g, 0.1 mol) was added dropwisely to a stirred methanol (20 mL) solution of 4-pyrazolylbenzaldehyde (1.72 g, 10 mmol) and acetophenone (1.20 g, 10 mmol) in a round-bottom flask at room temperature. The yellow solid product formed immediately. After filtration, the product was washed by methanol and water, dried in vacuo. Yield: 2.33 g, 85%. Anal. Calc. (%) for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21. Found (%): C, 78.53; H, 5.41; N, 10.46. ^{1}H NMR: (400 MHz, CD_3COCD_3), δ (ppm): 6.46 (s, 1H), 7.57, 7.59, 7.61 (t, J = 7.6 Hz, 2H), 7.67, 7.69, 7.71 (t, J = 7.6 Hz, 1H), 7.78 (s, 1H), 7.82, 7.80 (d, J = 7.6 Hz, 2H),

7.88 (s, 1H), 7.98, 8.02 (d, J = 15.6 Hz, 1H), 8.05, 8.07 (d, J = 8.4 Hz, 2H), 8.17, 8.19 (d, J = 7.6 Hz, 2H), 8.41 (s, 1H). IR ν(cm^{-1}): 653 (s), 699(s), 727 (m), 778 (s), 832 (s), 985 (s), 1019 (m), 1058 (s), 1108 (m), 1185 (m), 1219 (s), 1308 (s), 1336 (s), 1486 (m), 1552 (s), 1574 (s), 1600 (s), 1663 (s), 3093 (s). MS (EI) (*m/z*): Calc. for $C_{18}H_{14}N_2O$: 274.11 $[M]^+$; Found: 274.11 $[M]^+$.

Synthesis of B

4-Pyrazolylchalcone (2.00 g, 7.3 mmol), acetylpyridine (0.88 g, 7. 3 mmol) and NaOH (1.17 g, 29.2 mmol) were placed in a mortar. The mixture was ground for 30 min, then poured into distilled water (500 mL). The product was extracted twice with CH_2Cl_2, and the organic layer was dried overnight over anhydrous $MgSO_4$. The solvent was removed with a rotary evaporator to give the crude product. It was purified by recrystallization from ethanol. Yield: 2.16 g (75%). Anal. Calc. (%) for $C_{26}H_{22}N_2O_2$: C, 79.16; H, 5.62; N, 7.10. Found (%): C, 79.43; H, 5.41; N, 7.41. ^{1}H NMR: (400 MHz, CD_3COCD_3), δ (ppm): 3.52-3.60 (m, 3H), 3.94-4.00 (m, 1H), 3.76-3.82 (m, 1H), 6.49(s, 1H), 7.43, 7.45 (d, 2H), 7.49-7.53 (t, 2H), 7.60-7.69 (m, 5H), 7.88, 7.90 (d, 1H), 7.95, 8.00 (m, 3H), 8.39 (s, 1H), 8.71, 8.72 (d, 1H). MS (EI) (*m/z*): Calc. for $C_{26}H_{22}N_2O_2$: 395.17 $[M]^+$; Found: 395.16 $[M]^+$. IR ν(cm^{-1}): 558 (s), 690 (s), 753 (s), 778 (s), 825 (s), 846 (w), 940 (s), 992 (s), 1033 (m), 1057 (m), 1182 (w), 1212 (m), 1231 (s), 1334 (m), 1365 (s), 1397 (s), 1450 (w), 1525 (s), 1582 (m), 1677 (s), 1702 (s), 3135 (w).

Synthesis of 6-phenyl-4-(4-(1H-pyrazolyl)phenyl)-2, 2´-bipyridine (L)

Compound **B** (1.0 g, 2.53 mmol), NH_4OAc (1.95 g, 25.3 mmol) and ethanol (25 mL) were added to a round-bottom flask. The reaction mixture was kept stirring for 10 h at 85 ^oC. After cooled to room temperature, it was poured into distilled water (100 mL). The product was extracted twice with CH_2Cl_2, and the organic layer was dried overnight over anhydrous $MgSO_4$. The solvent was removed with a rotary evaporator to give the crude product. It was purified by recrystallization from ethanol. Yield: 0.378 g (40%). Anal. Calc. for $C_{25}H_{18}N_4$: C, 80.19; H, 4.85; N, 14.96. Found: C, 80.43; H, 4.55; N, 14.63%. ^{1}H NMR: (400 MHz, CD_3COCD_3), δ (ppm): 6.62 (s, 1H), 7.50-7.60 (m, 4H), 7.82 (s, 1H), 8.16, 8.18 (d, 2H), 8.38-8.41 (m, 3H), 8.64-8.68

(m, 3H). 8.77, 8.78 (d, 1H). MS (EI) (*m/z*): Calc. for $C_{25}H_{18}N_4$: 374.15 $[M]^+$; Found: 374.15 $[M]^+$. IR ν(cm^{-1}): 691(s), 745(s), 793(s), 828(s), 832(s), 935(s), 1043(s), 1121(m), 1201(m), 1337(w), 1389(s), 1451(w), 1472(w), 1526(s), 1548(m), 1601(s), 1663(s), 3053(w). Needle–like crystals of polymorph **I** were grown from the methanol solution by slow evaporation at room temperature, and crystals of polymorph **II** were obtained from the mixture of ligand and AgSCN methanol solution or methanol/dichloromethane mixed solution by slow evaporation at room temperature over several days.

Table S1 Crystal Date and Refinement of Polymorphs **I** and **II** of Ligand and Complexes **1-3**

Compound	Form **I**	Form **II**	Complex **1**	Complex **2**	Complex **3**
empirical formula	$C_{25}H_{18}N_4$	$C_{25}H_{18}N_4$	$C_{64}H_{50}Ag_2N_8O_6S_2$	$C_{50}H_{36}Ag_2Cl_2N_8O_8$	$C_{150}H_{108}Ag_4N_{28}O_{16}$
formula weight	374.43	374.43	1306.98	1163.51	2990.12
crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
space group	$P2_1/c$	$P2_1$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a [Å]	19.434(5)	11.090(2)	9.731(2)	16.63(4)	12.745(5)
b [Å]	5.479(5)	7.422(3)	11.700(2)	22.03(5)	13.971(5)
c [Å]	17.999(5)	22.999(2)	13.496(3)	25.70(6)	21.091(5)
α [°]	90.00	90.00	77.46(3)	90.00	101.276(5)
β [°]	92.686(5)	92.998(4)	81.25(3)	119.395(5)	93.521(5)
γ [°]	90.00	90.00	68.07(3)	90.00	114.371(5)
V [$Å^3$]	1914(2)	1890.5(9)	1387.1(5)	4718(2)	3312(2)
Z	4	4	1	4	1
T [K]	298(2)	298(2)	298(2)	298(2)	298(2)
D calcd [g ·cm^{-3}]	1.299	1.316	1.565	1.638	1.499
μ [mm^{-1}]	0.079	0.080	0.844	1.008	0.661
F(000)	784	784	664	2336	1520
θ range [°]	1.05-25.00	0.89-25.05	1.55-25.00	1.68-25.00	1.00-25.05
total no. data	10979	13570	9949	16594	23791
no.unique data	3375	5864	4862	4174	11581
no. params refined	313	523	381	317	920
R (int)	0.0238	0.0312	0.0145	0.0670	0.0400
R_1 [$I > 2\sigma(I)$]	0.0462	0.0430	0.0263	0.0435	0.0574
wR_2 [$I > 2\sigma(I)$]	0.1432	0.0938	0.0626	0.0839	0.1570
R_1 (all data)	0.0597	0.0702	0.0309	0.1095	0.1054
wR_2 (all data)	0.1668	0.1164	0.0653	0.1078	0.1886
GOF on F^2	1.059	1.023	1.042	0.998	1.038

Table S2 Selected Bond Lengths (Å) and Angles (°) of Complexes **1**-**3**

Complex **1**			
Ag(1)–N(4)#1	2.249(2)	N(4)#1–Ag(1)–N(2)	122.44(6)
Ag(1)–N(1)	2.313(2)	N(1)–Ag(1)–N(2)	71.05(6)
Ag(1)–N(2)	2.385(2)	N(4)#1–Ag(1)–O(3)	91.72(7)
Ag(1)–O(3)	2.511(2)	N(1)–Ag(1)–O(3)	117.16(6)
N(4)#1-Ag(1)-N(1)	132.11(7)	N(2)–Ag(1)–O(3)	126.79(7)
Complex **2**			
Ag(1)–N(2)#1	2.178(4)	N(2)#1–Ag(1)–N(4)	152.1(2)
Ag(1)–N(4)	2.249(4)	N(2)#1–Ag(1)–N(3)	126.0(2)
Ag(1)–N(3)	2.453(4)	N(4)–Ag(1)–N(3)	71.4(2)
Complex **3**			
Ag(1)–N(2)	2.217(5)	Ag(1)–N(6)	2.231(4)
Ag(1)–N(5)	2.404(4)	Ag(1)–N(1)	2.450(4)
Ag(2)–N(12)#1	2.232(5)	Ag(2)–N(9)	2.297(5)
Ag(2)–N(10)	2.399(5)	Ag(2)–O(1)	2.55(2)
N(2)–Ag(1)–N(6)	151.6(2)	N(2)–Ag(1)–N(5)	134.0(2)
N(6)–Ag(1)–N(5)	71.9(2)	N(2)–Ag(1)–N(1)	71.5(2)
N(6)–Ag(1)–N(1)	126.7(2)	N(5)–Ag(1)–N(1)	91.9(1)
N(12)#1–Ag(2)–N(9)	133.5(2)	N(12)#1–Ag(2)–N(10)	123.8(2)
N(9)–Ag(2)–N(10)	70.4(2)	N(12)#1–Ag(2)–O(1)	99.1(5)
N(9)–Ag(2)–O(1)	112.2(4)	N(10)–Ag(2)–O(1)	117.8(5)

Symmetry transformations used to generate equivalent atoms. For **1**: #1 -x,-y+1,-z+2 ; For **2**: #1 -x,-y+2,-z+2; For **3**: #1 -x+2,-y+1,-z+2

Table S3 The dihedral angles between the neighboring connected aromatic rings in structures of two polymorphs and the ligand in complexes.

	polymorph **I**	polymorph **II**	Complex **1**	Complex **2**	Complex **3**
Angle (1-2) [°]	8.29	10.11/3.10	34.82	39.35	34.28/28.63
Angle (2-3) [°]	13.88	22.74/35.94	25.71	11.45	19.47/22.39
Angle (3-4) [°]	9.85	7.32/13.98	16.28	22.93	6.89/3.86
Angle (3-5) [°]	2.30	22.17/27.21	35.07	23.58	38.17/44.50

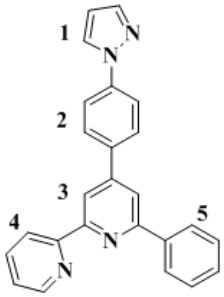

Table S4. Third-order NLO date for **L** and complexes **2** and **3**

Compound	**L**	Complex **2**	Complex **3**
β (cm GW^{-1})	0.556	1.428	1.093
σ (cm^4 s photon^{-1} molecular^{-1})	2.483×10^{-46}	6.369×10^{-46}	4.875×10^{-46}
γ (m^2 W^{-1})	3.441×10^{-18}	3.361×10^{-18}	3.151×10^{-18}
$\chi^{(3)}$ (esu)	1.709×10^{-15}	2.142×10^{-15}	3.345×10^{-15}

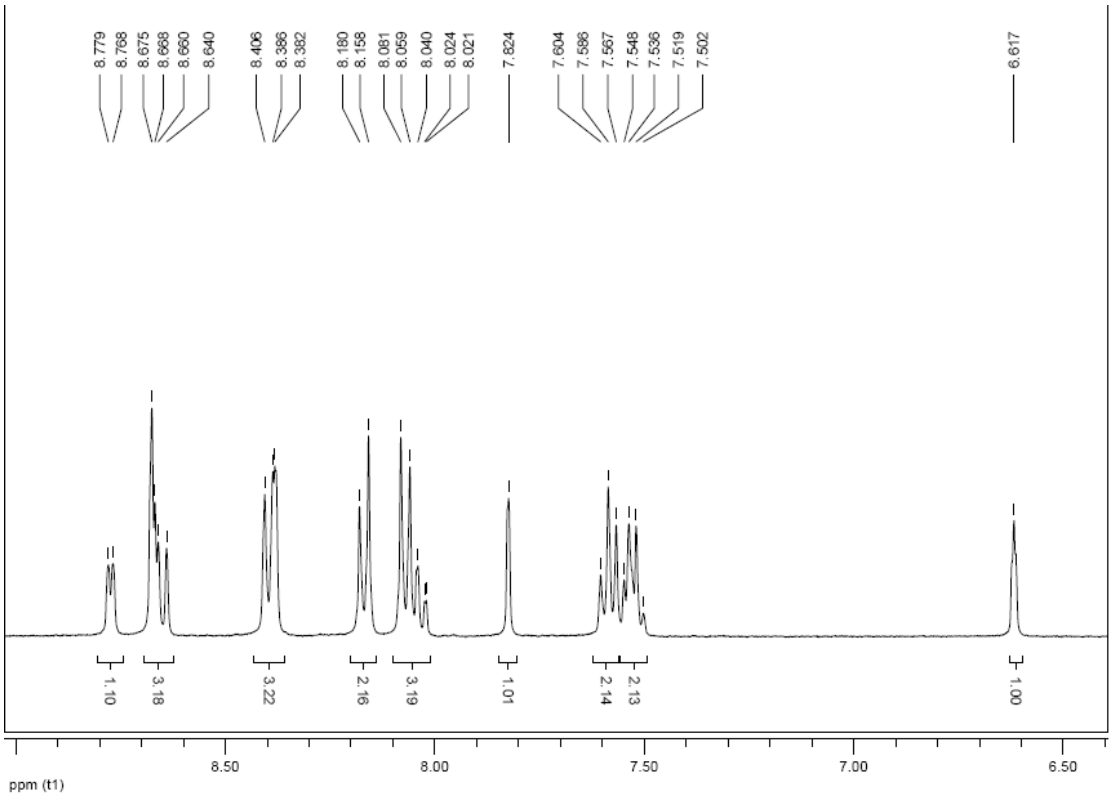

Figure S1 ^{1}H NMR spectrum of **L**.

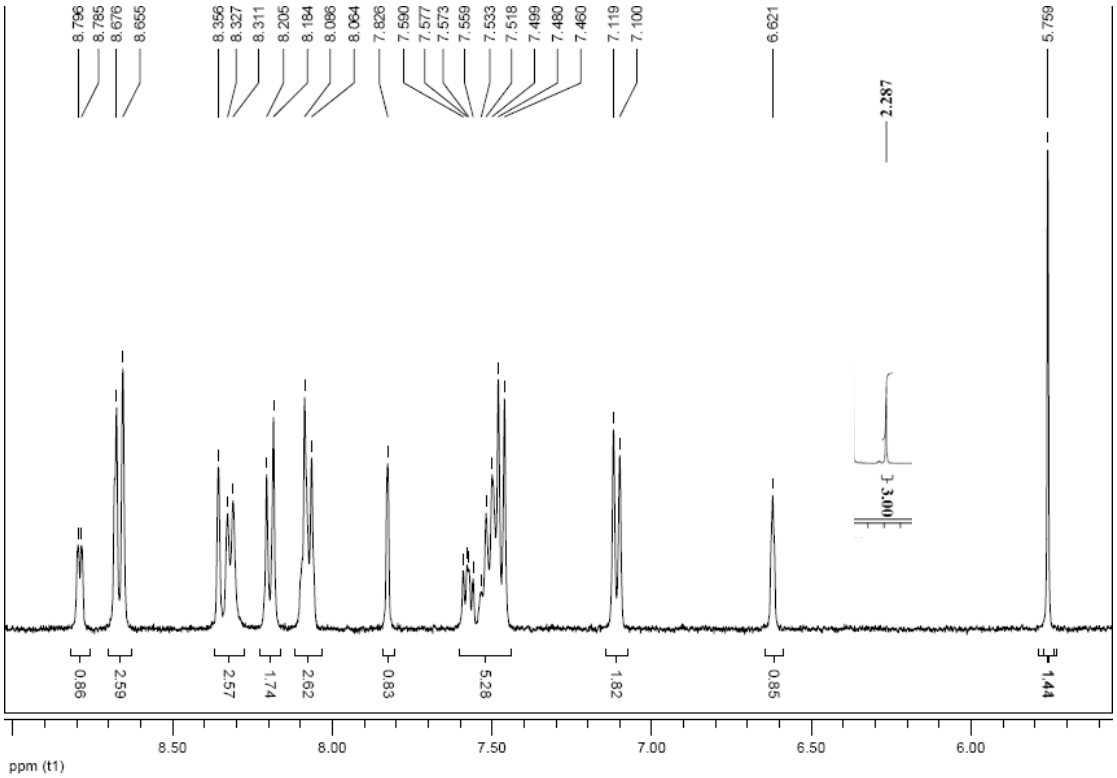

Figure S2 ^{1}H NMR spectrum of complex **1**.

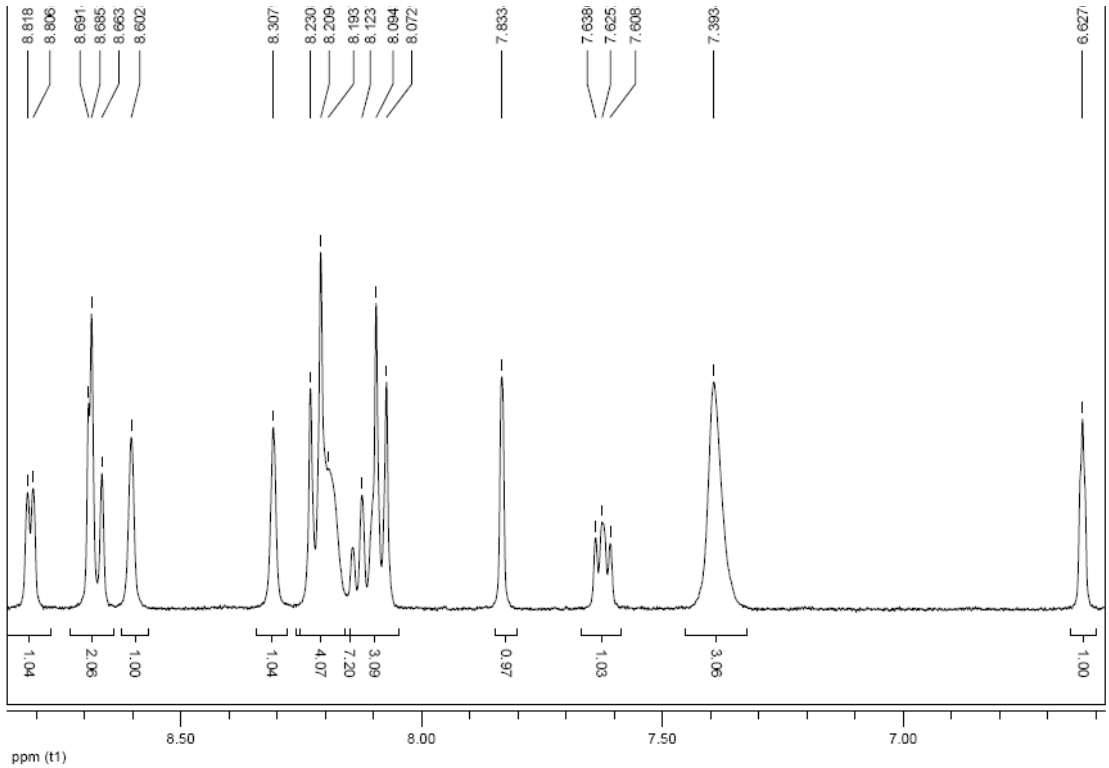

Figure S3 ^{1}H NMR spectrum of complex **2**.

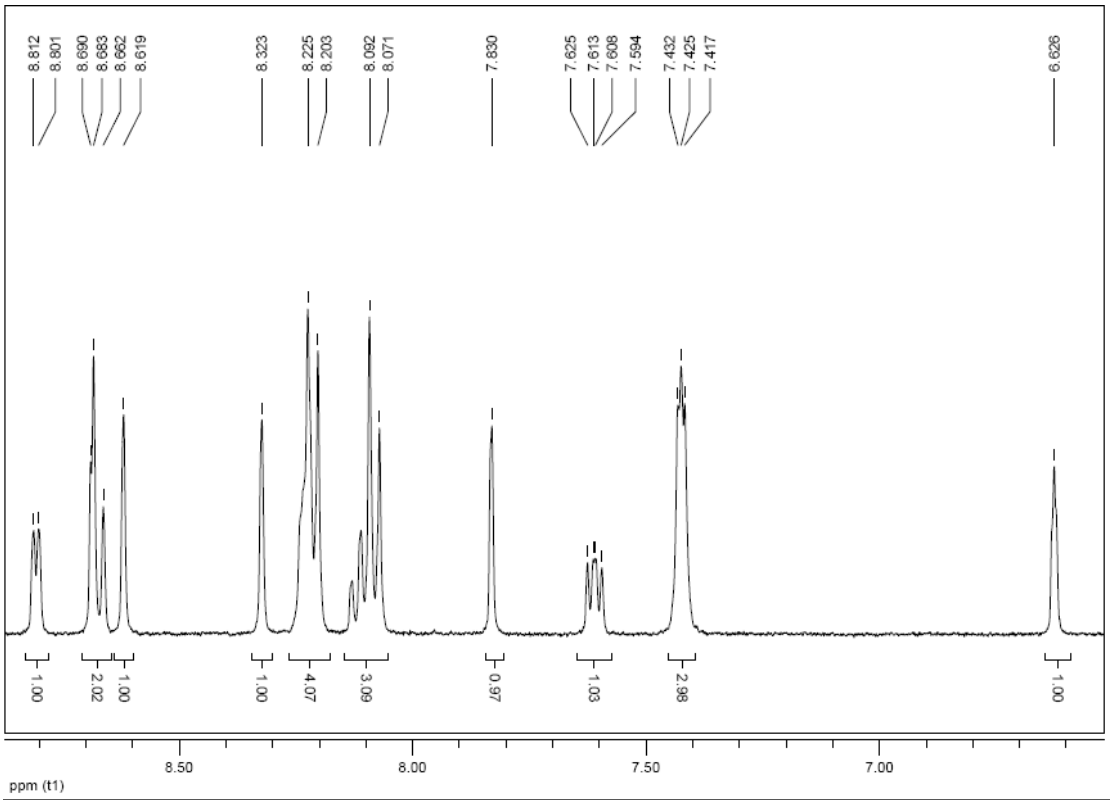

Figure S4 ^{1}H NMR spectrum of complex **3**.

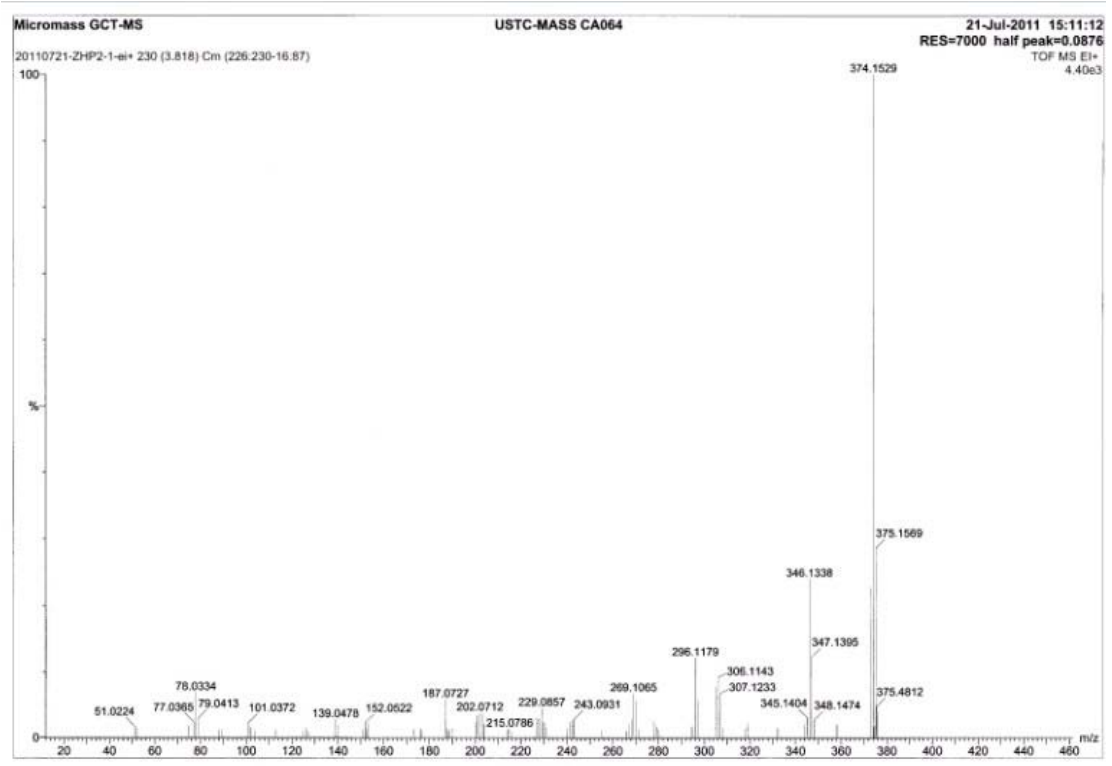

Figure S5 MS of **L**

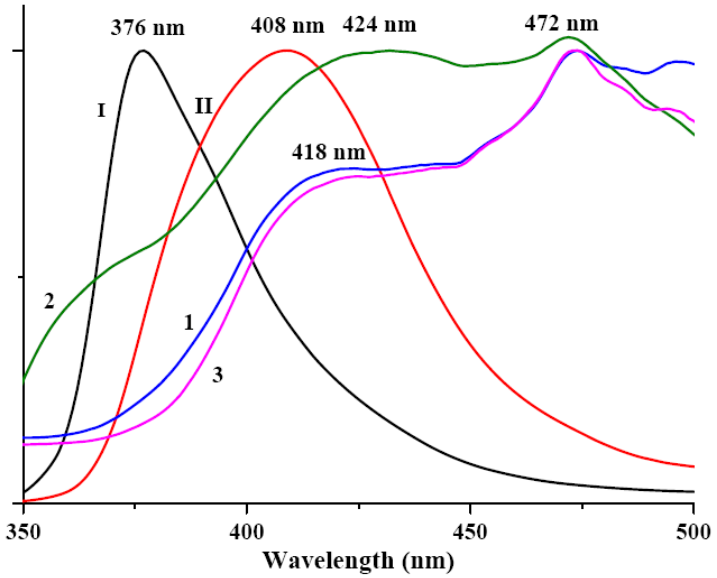

Figure S6 Solid-state emission spectra of polymorphs **I**, **II** and complexes **1**-**3** at room temperature.

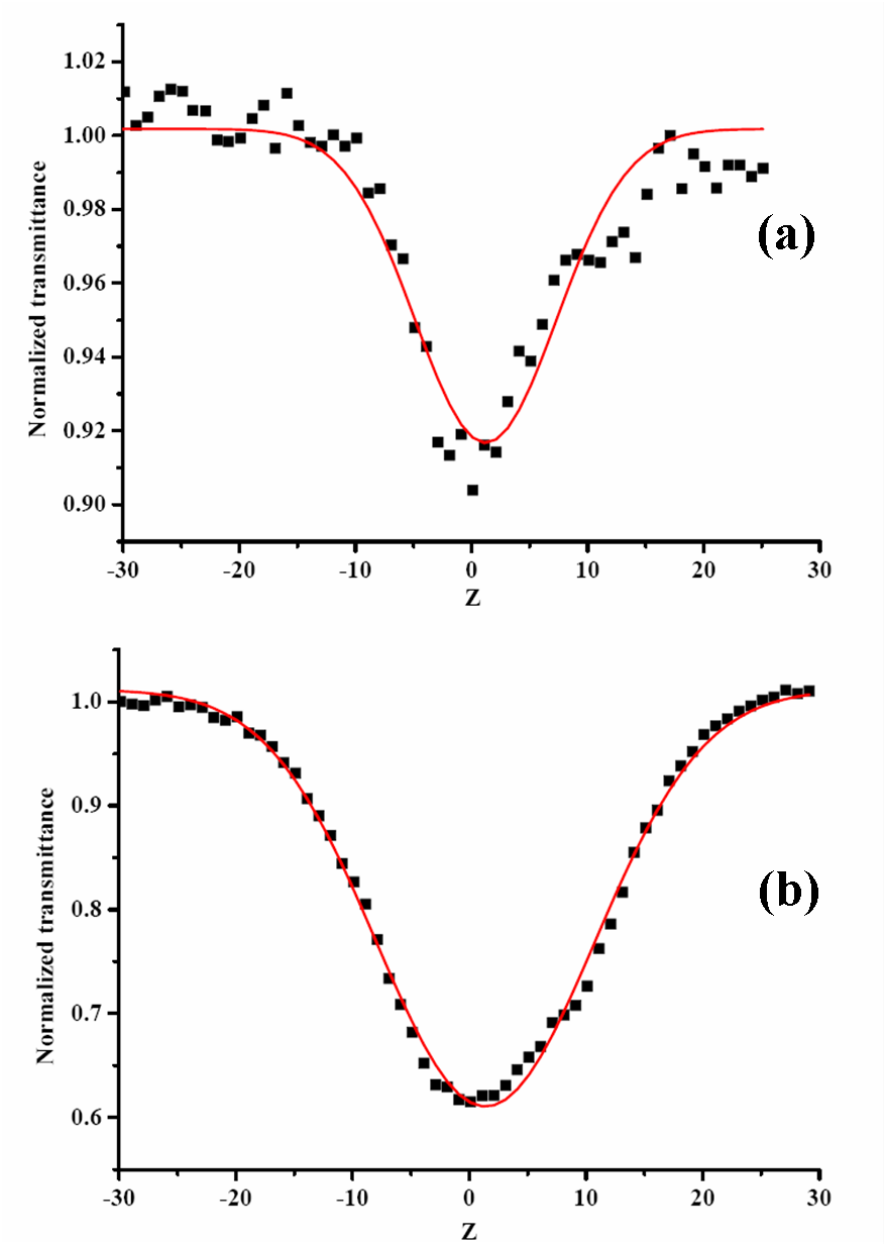

Figure S7 The open aperture Z-scan data of (a) **L** and (b) complex **2**. The filled squares represent the experimental data and the solid curve is the theoretical data.

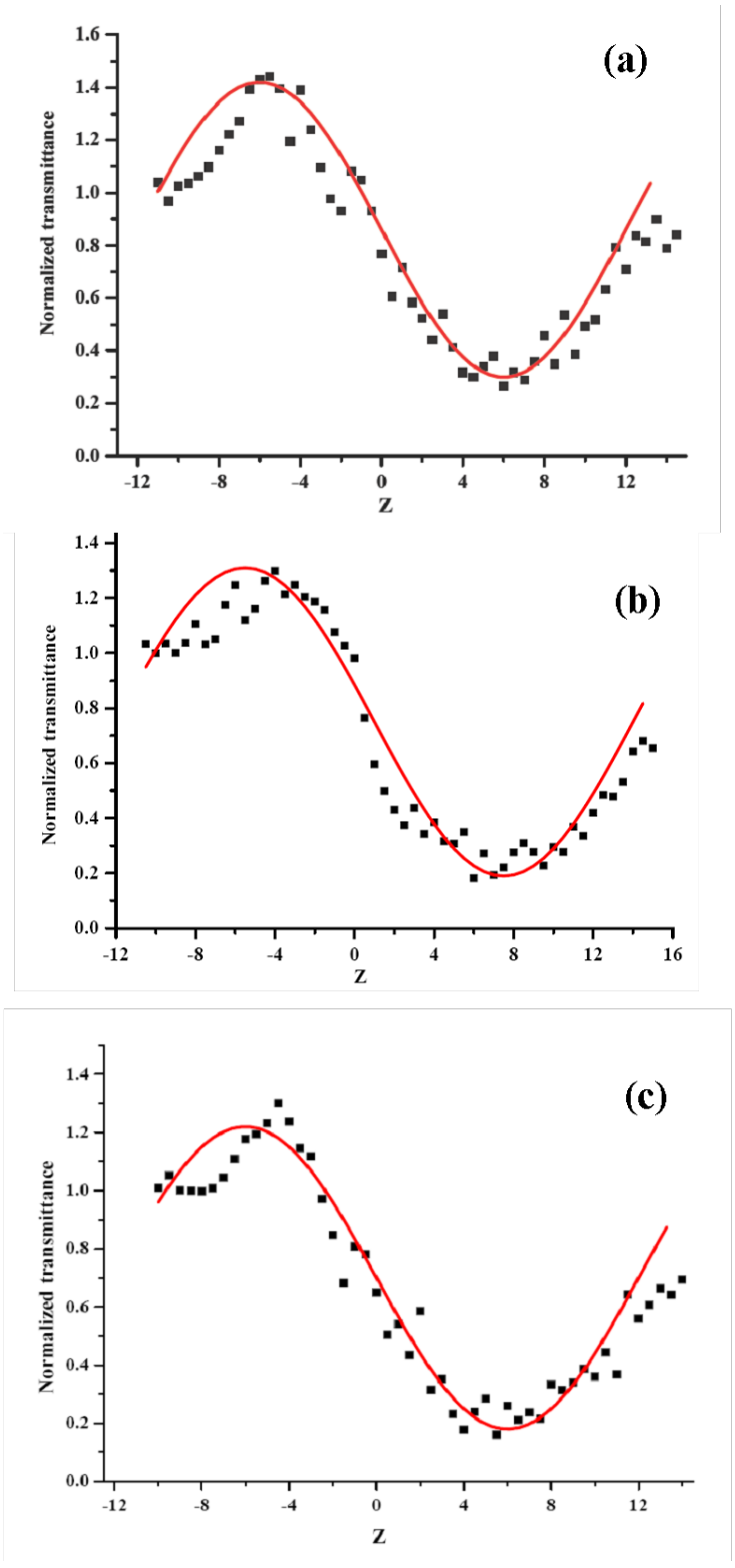

Figure S8 The closed aperture Z-scan data of (a) **L**, (b) complex **2** and (c) complex **3**. The filled squares represent the experimental data and the solid curve is the theoretical data.