Supporting Information

Solid state emissive azo-schiff base ligands and their Zn(II) complexes: acidochromism and photoswitching behaviour

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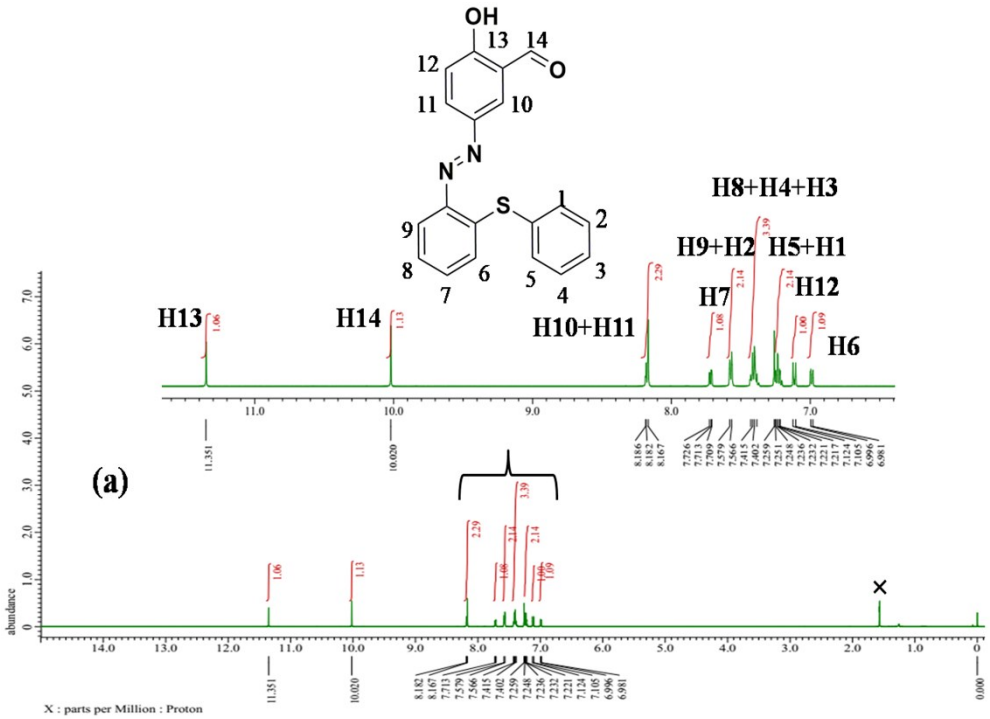


Fig. S1 ^{1}H NMR spectra of **1.**

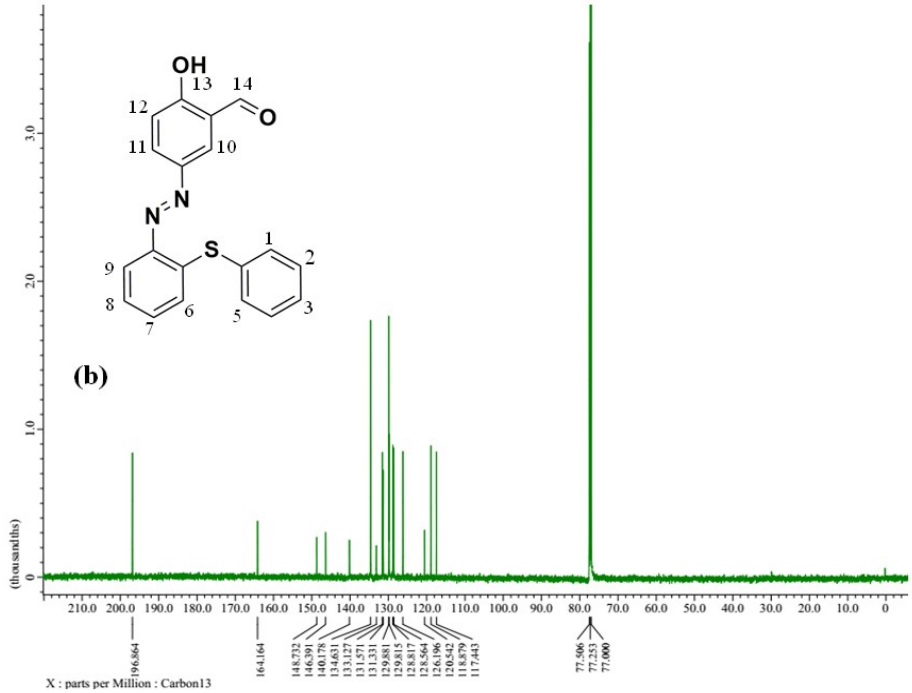


Fig. S2 ^{13}C (b) NMR spectra of **1**.

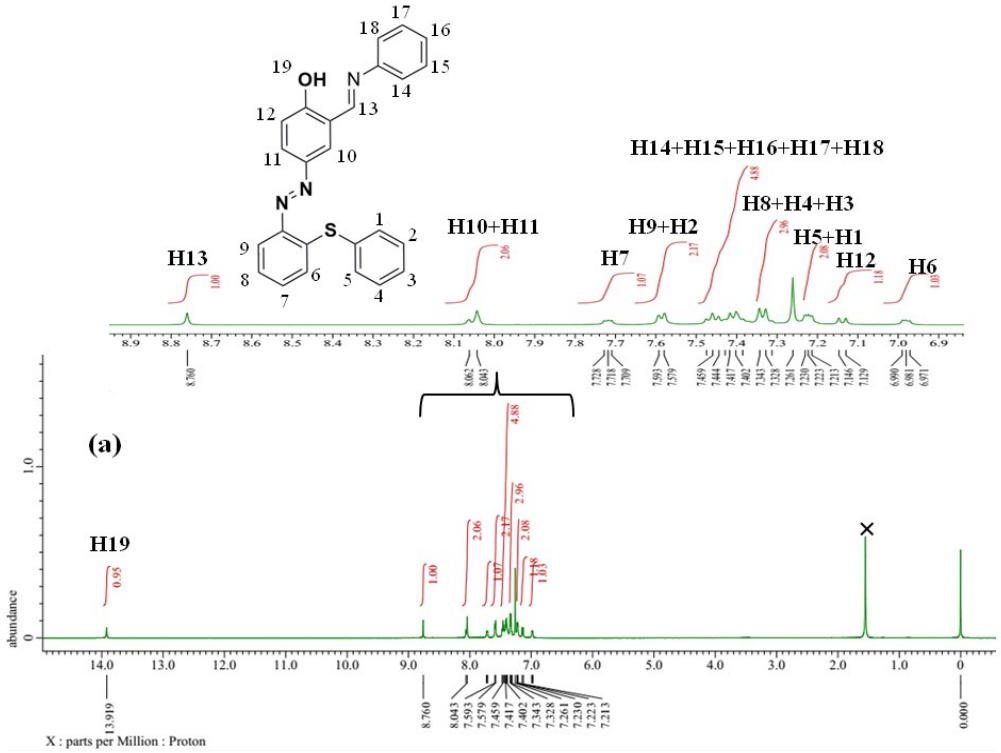


Fig. S3 ^{1}H NMR spectra of **L1**.

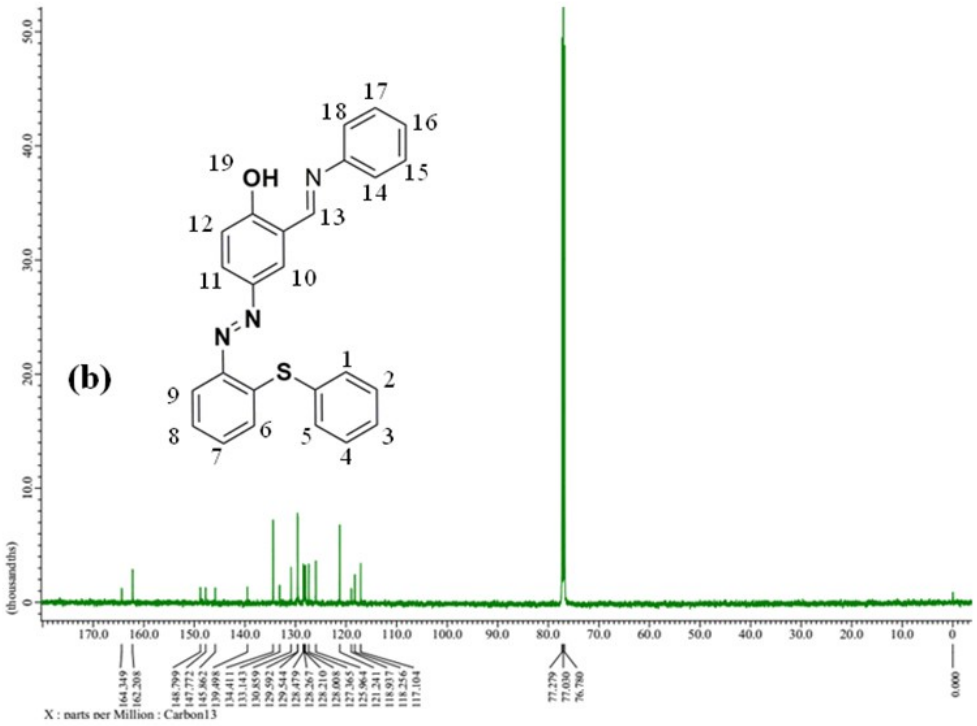


Fig. S4 ^{13}C (b) NMR spectra of **L1**.

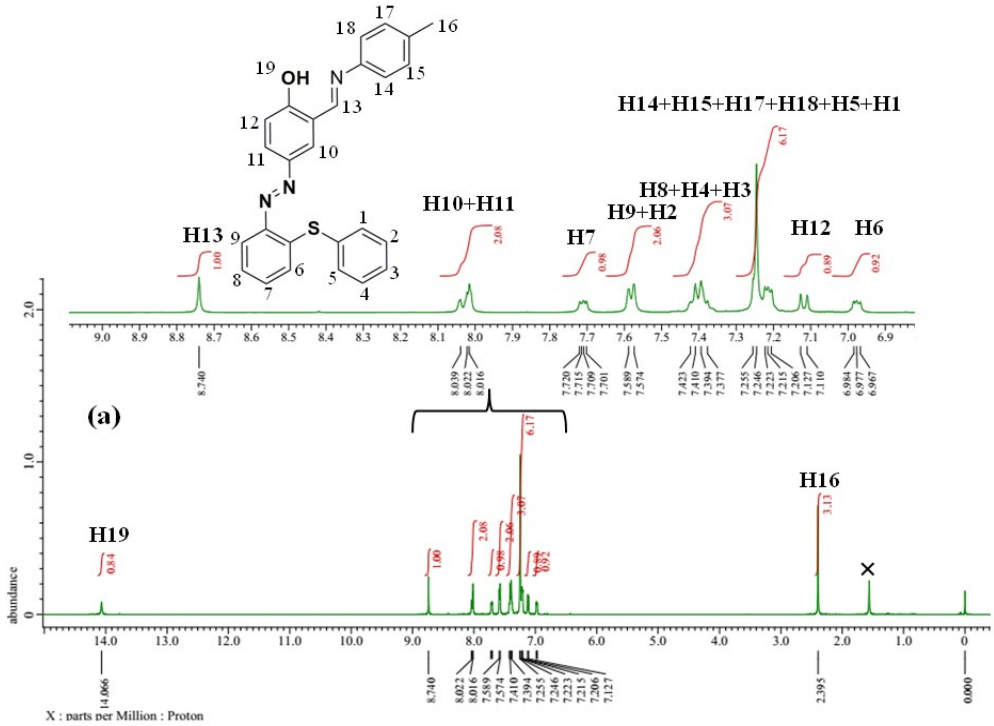


Fig. S5 ^{1}H (a) NMR spectra of **L2**.

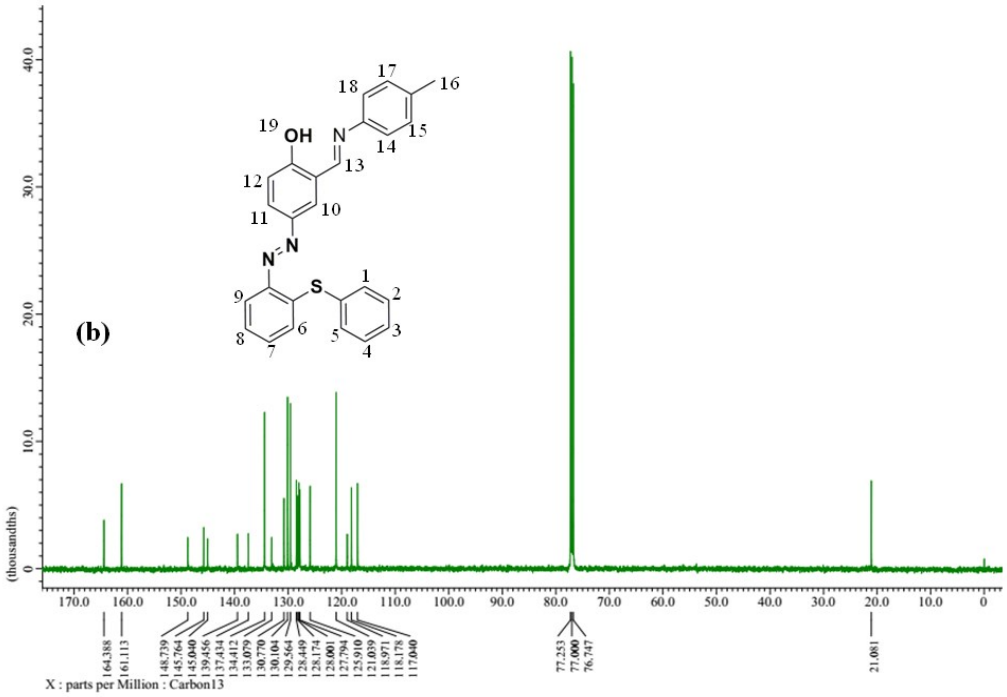
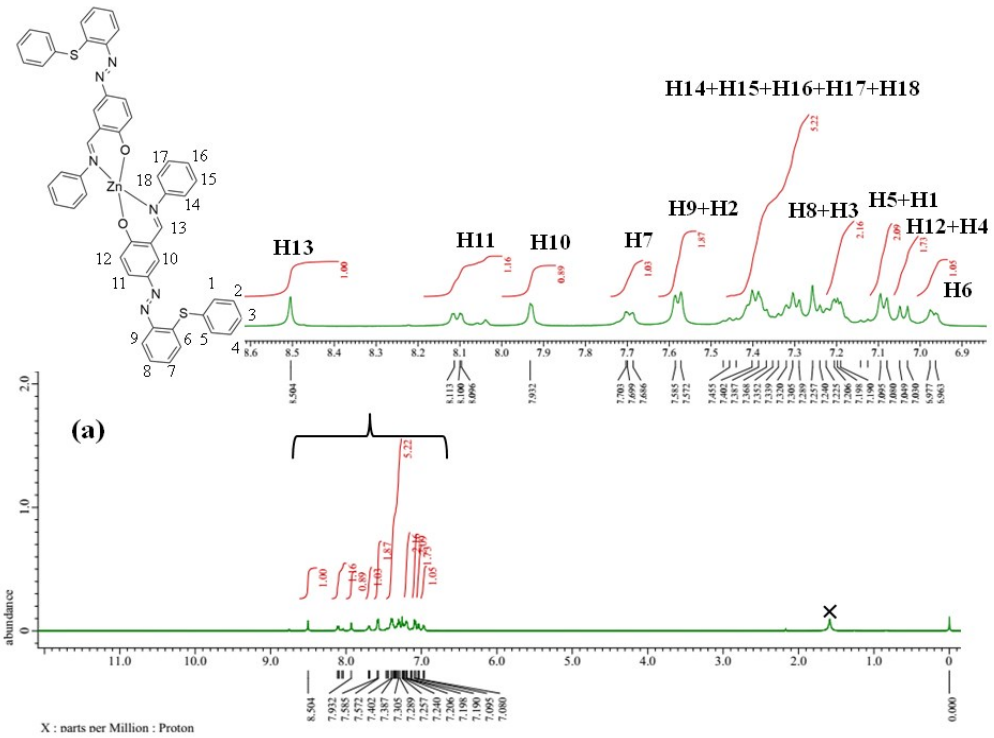


Fig. S6 ^{13}C (b) NMR spectra of **L2**



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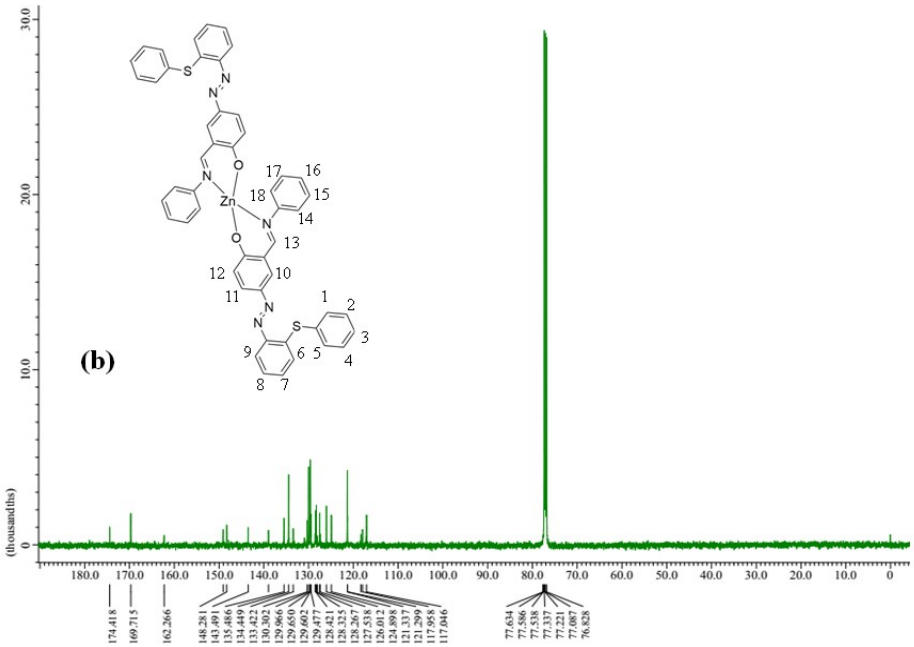


Fig. S8 ^{13}C (b) NMR spectra of **C1**

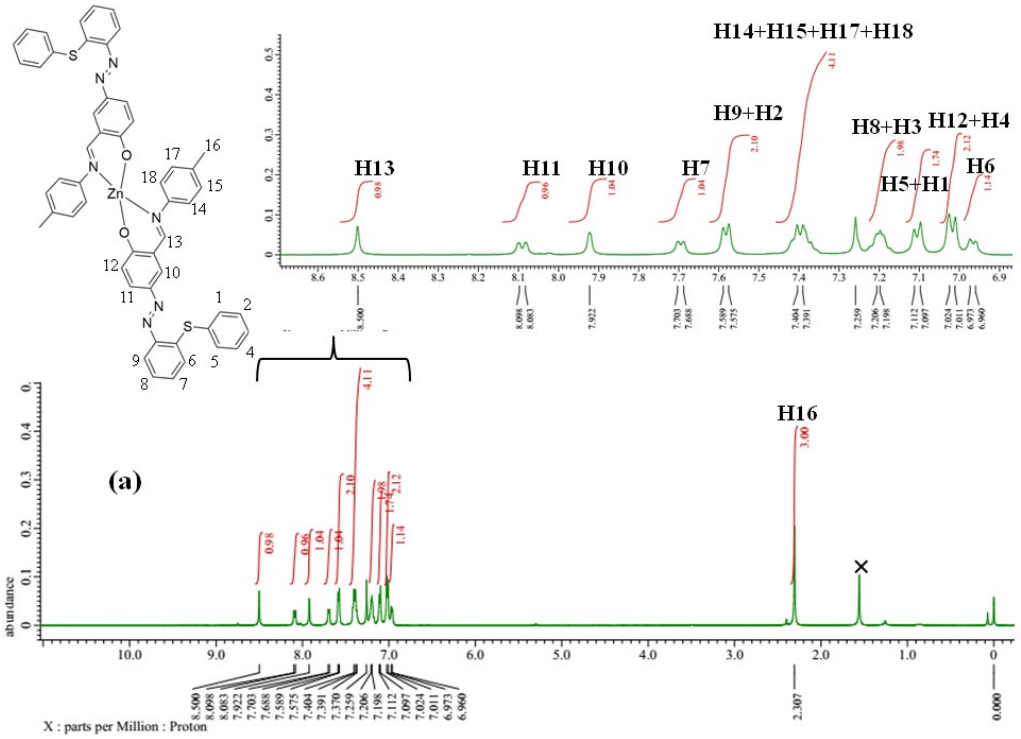


Fig. S9 ^{1}H (a) NMR spectra of **C2**

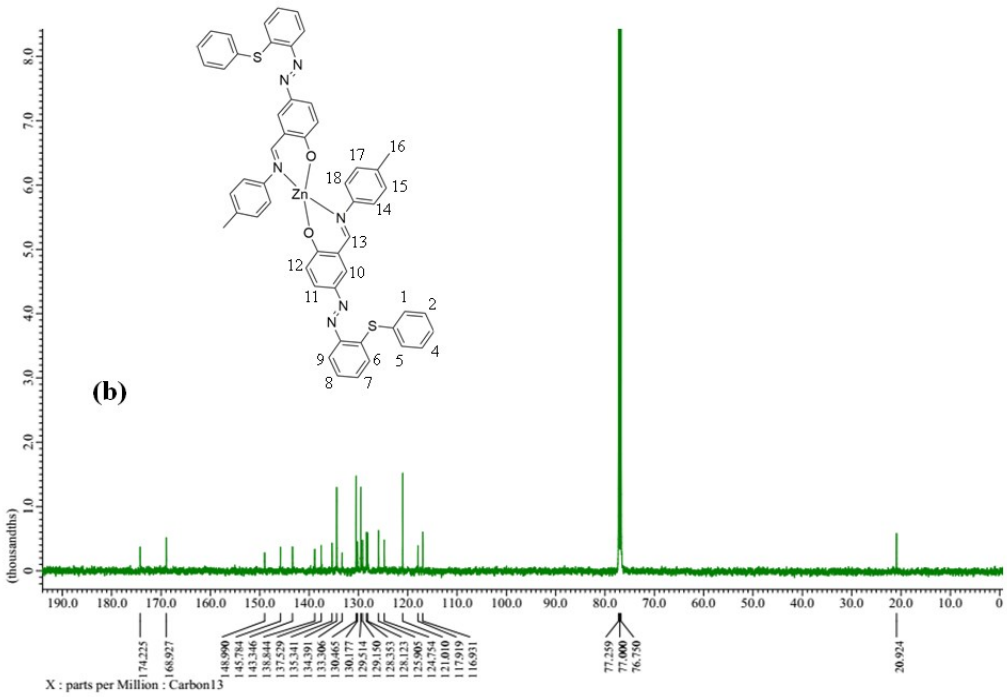


Fig. S10 ^{13}C (b) NMR spectra of **C2**

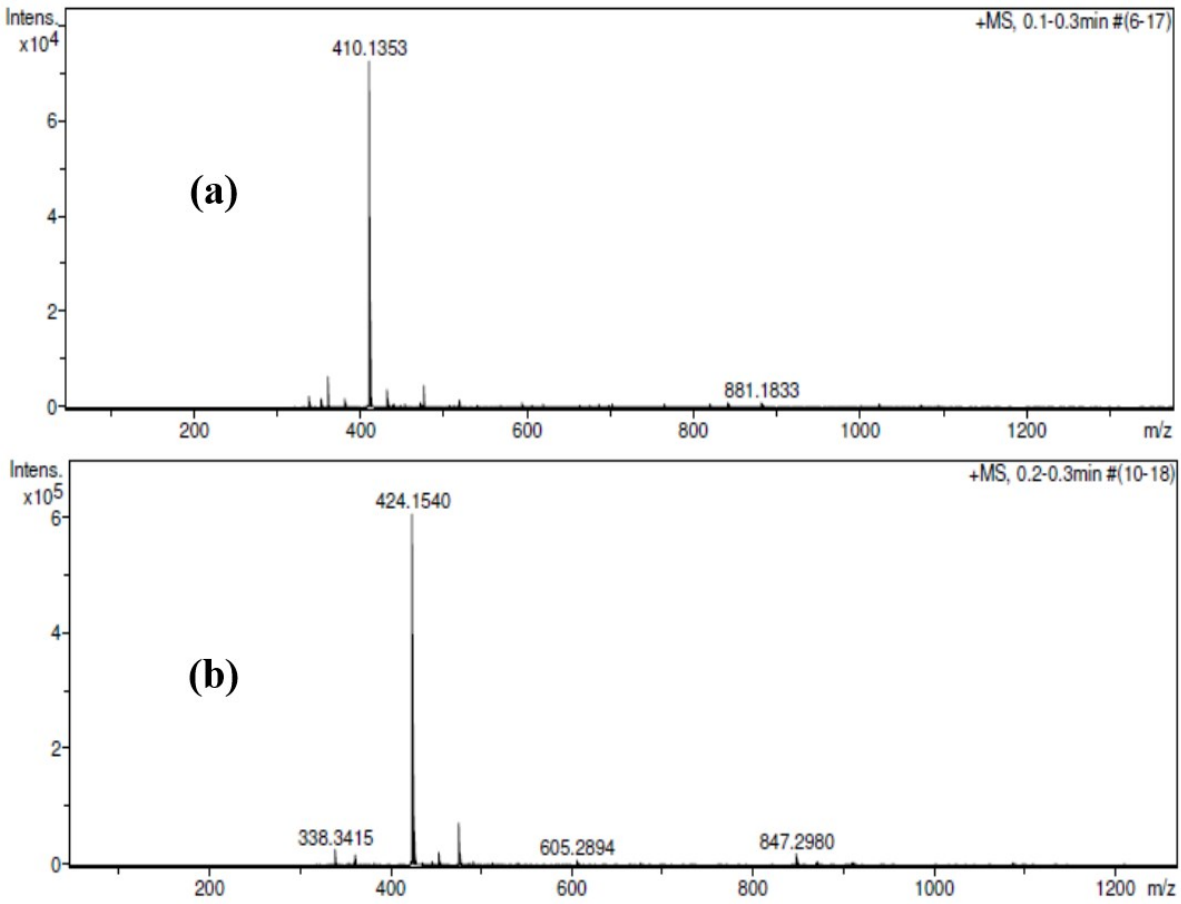
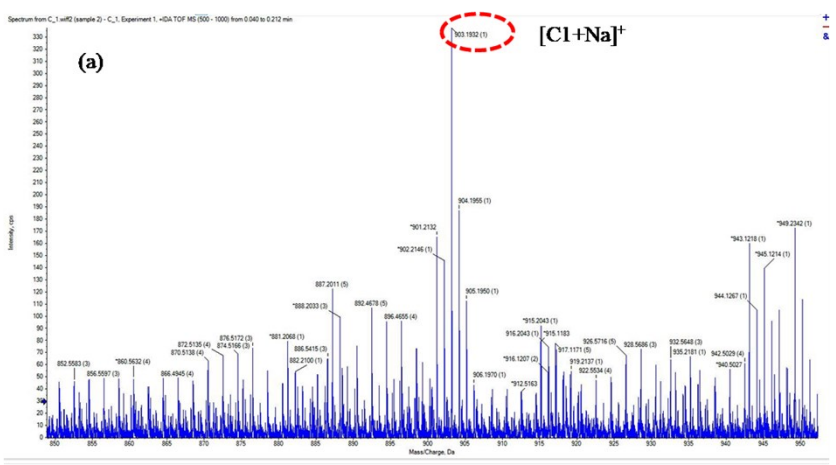


Fig. S11 ESI-MS spectra of **L1** (a) and L**2** (b).



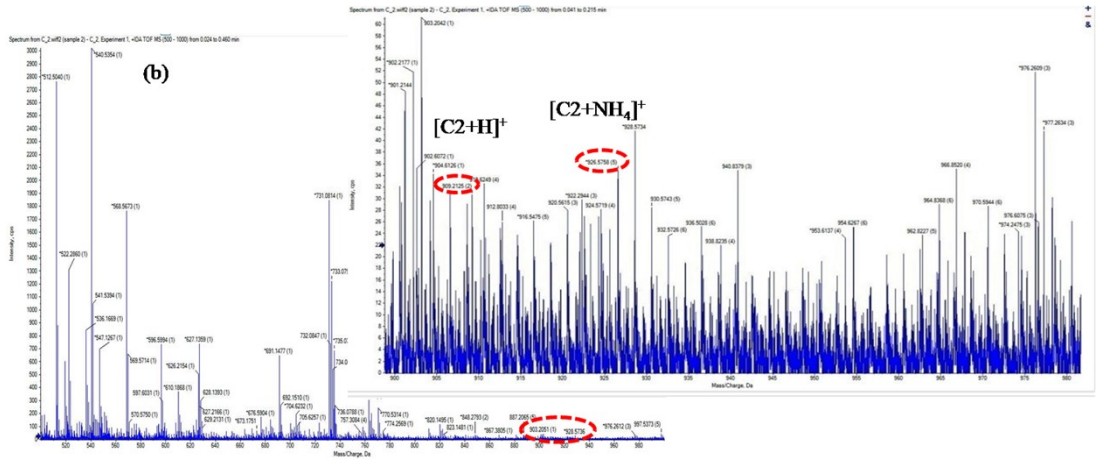


Fig. S12 ESI-MS spectra of **C1** (a) and **C2** (b).

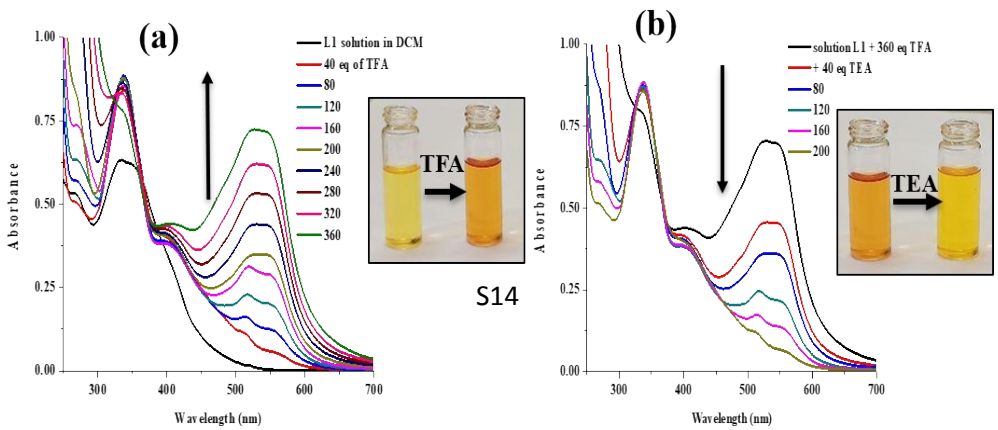


Fig. S13 Change in UV/vis absorption spectra for the dichloromethane solution of **L2** under titration of (a) TFA and also (b) TEA

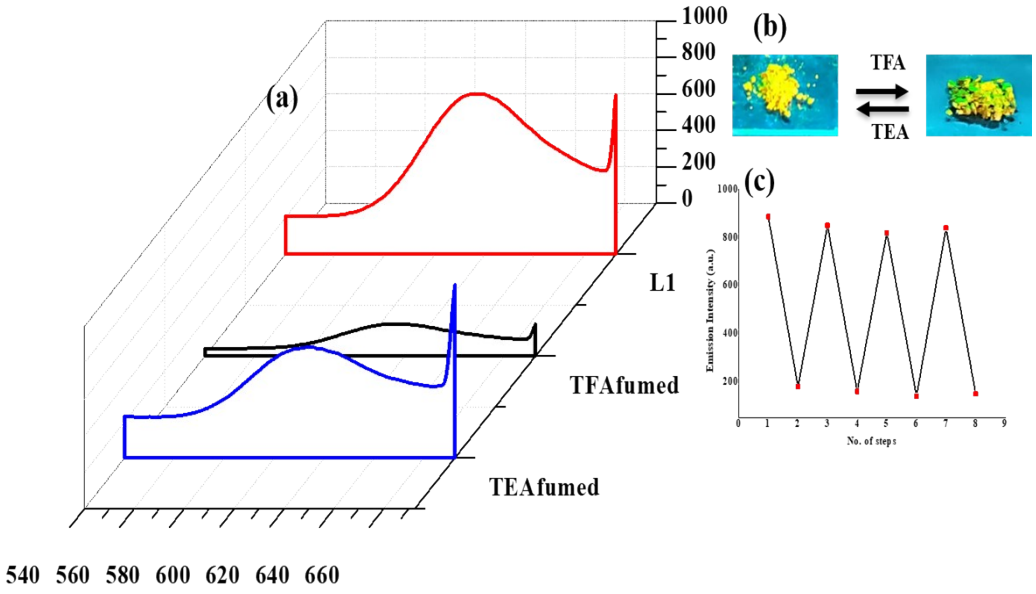


Fig. S14 Change in solid–state emission spectrum of **L1** upon exposure to TFA fumes and regain the solid- state emission spectrum with exposure by TEA fumes (a), and photographs (b) emission switch cycle upon exposure to TFA and TEA(c).

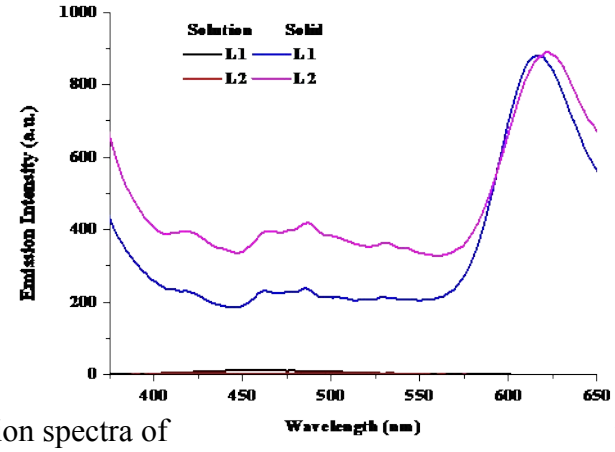
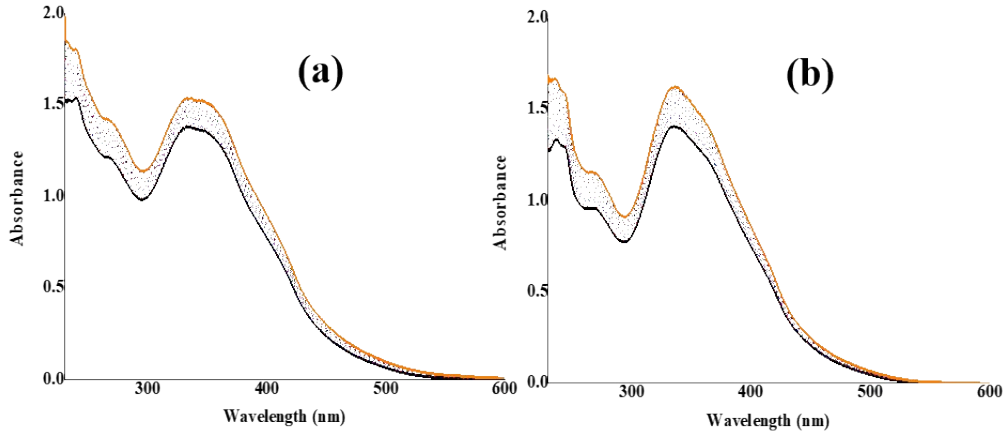


Fig. S15 Emission spectra of the ligands L1 and L2 in solution and solid.



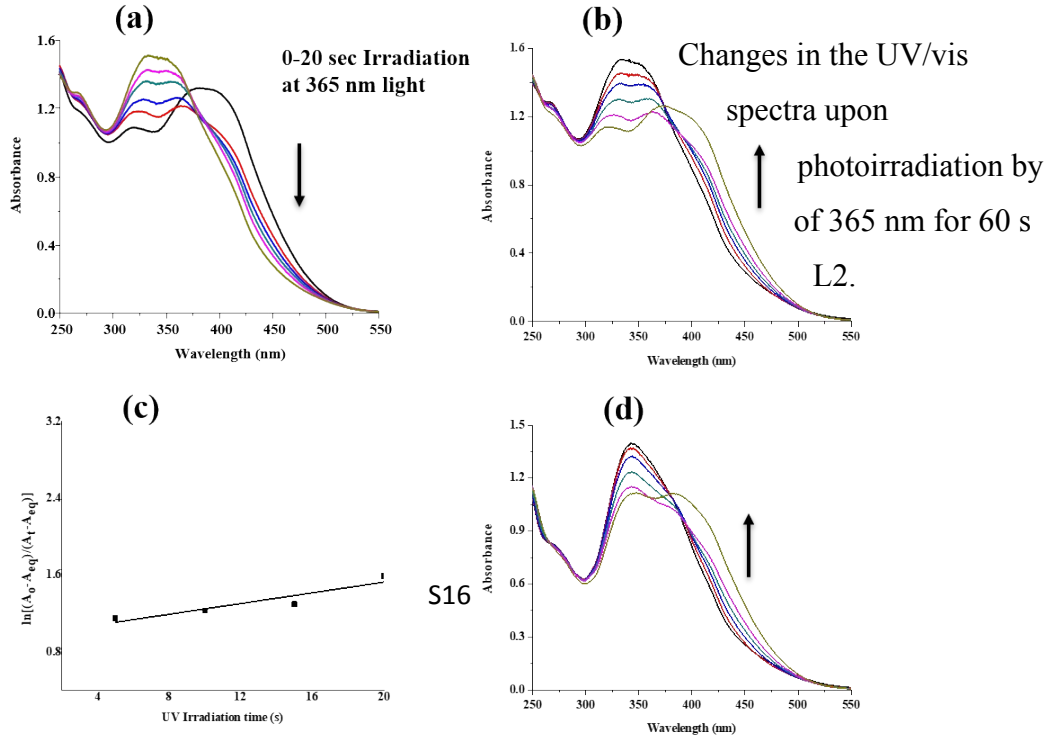


Fig. S16 Changes in the UV/vis absorption spectra upon photoirradiation by UV light of 365 nm for 60 s (a) L1, (b) L2.

Fig. S17 Changes in the UV/vis absorption spectra upon photoirradiation by UV light of 365 nm for 20 s *trans* to *cis* (a), *cis* to *trans* (b), photoisomerization kinetics of the complex **C1**, UV/vis spectra obtained during UV (λ_{max}, 395 nm) (c), *cis* to *trans* for **C2** (d)

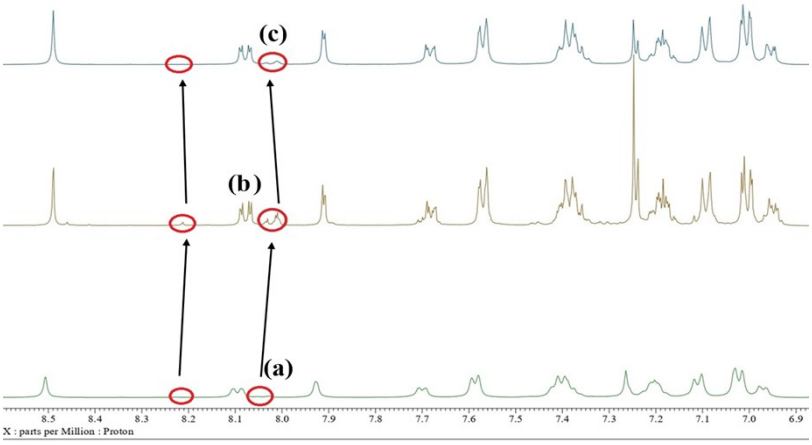


Fig. S18 ^{1}H NMR spectral changes in the aromatic region of L2 in $CDCl_3$ upon irradiation with UV light (365 nm) (a) spectrum of *trans*-**L2** before irradiation; (b) after irradiation for 15 s and (c) after keeping in the dark for 24 h.

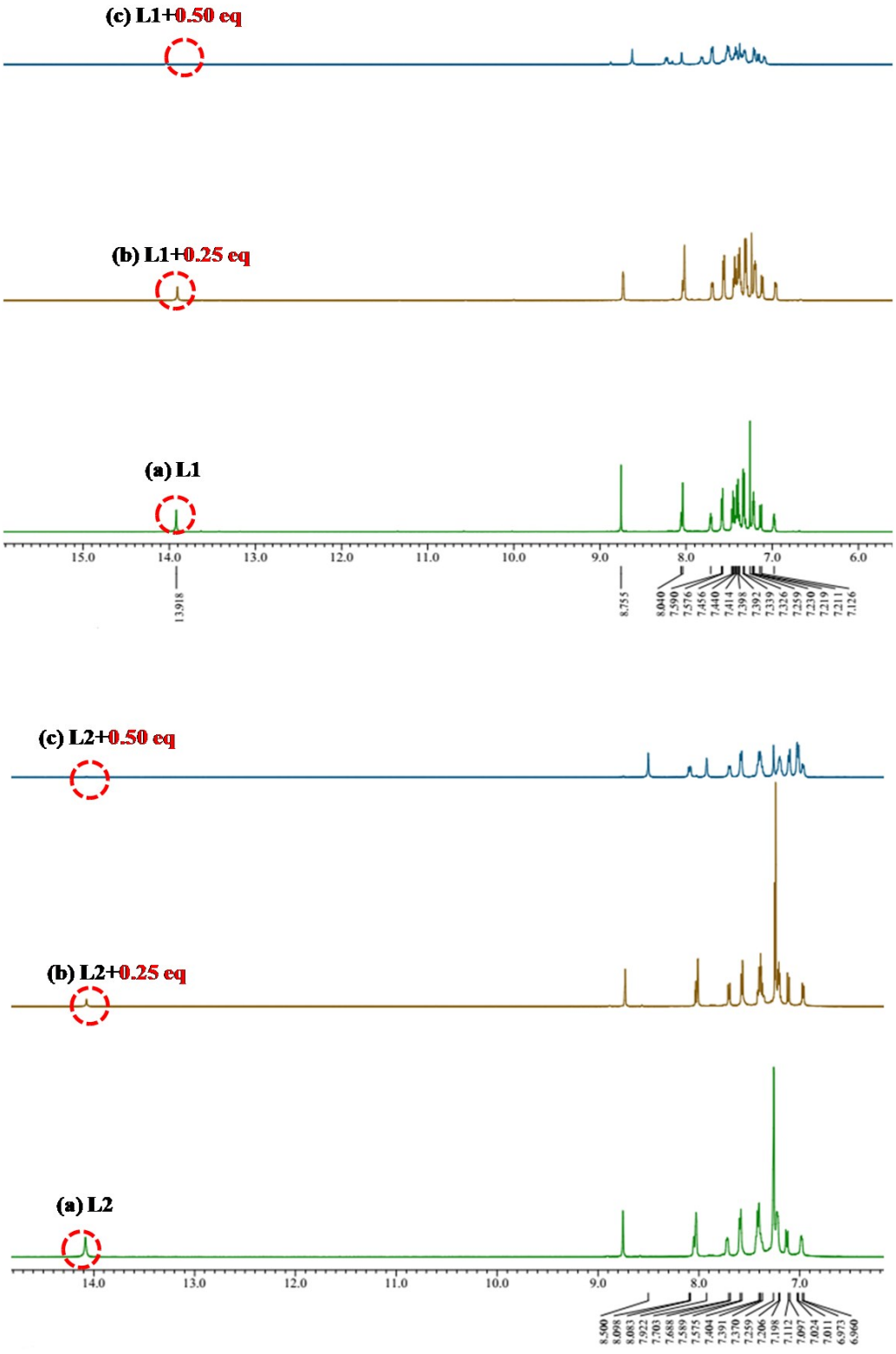
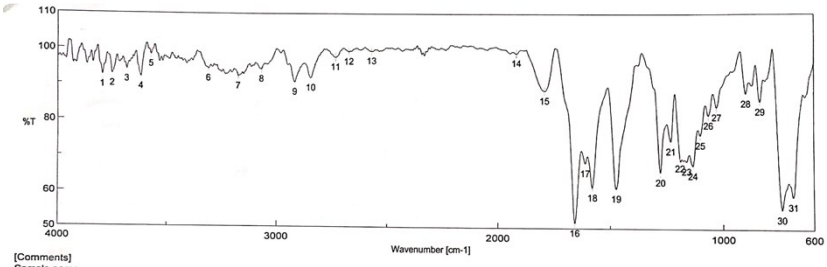


Fig. 19 ^{1}H NMR titration of L1 by Zn^{2+} (a) and L2 (b)



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Comment
User Amit Kumar Singh
Division Chemistry
Company BHU

[Result of Peak Picking]

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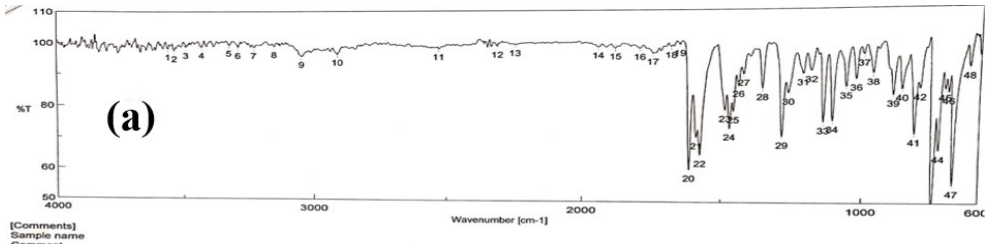
5	3577.31	98.223	6	3315.03	94.2535	7	3179.08	92.0995	8	3073.01	94.0615
9	2920.66	90.4021	10	2847.38	91.5517	11	2735.53	97.4375	12	2674.78	98.9865
13	2571.61	99.1417	14	1916.9	98.6577	15	1791.55	88.0292	16	1657.52	51.4548
17	1611.23	67.977	18	1579.41	61.2667	19	1473.35	61.0192	20	1277.61	65.5696
21	1230.36	74.1804	22	1190.83	69.5322	23	1161.9	68.6222	24	1133.94	67.4265
25	1100.19	75.8496	26	1063.55	81.372	27	1026.91	83.6417	28	898.666	87.5053
29	836.955	85.26	30	740.531	55.397	31	691.355	58.9387			

Fig. S20 IR spectrum of **1**



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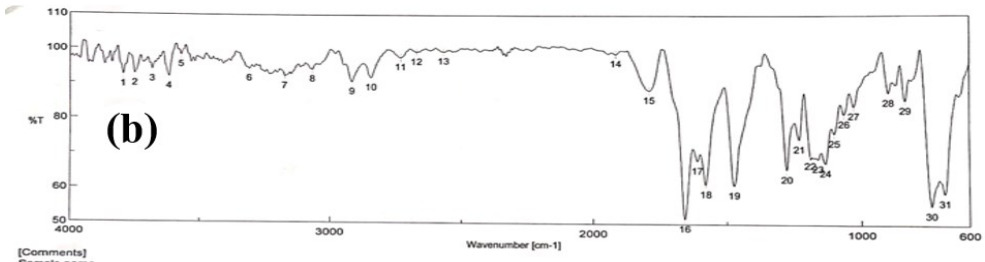
13	2252.45	99.1039	14	1946.31	98.3025	15	1884.11	97.9626	16	1794.92	97.8263
17	1747.19	96.2714	18	1681.14	98.4076	19	1649.32	98.9953	20	1614.61	60.042
21	1589.06	70.0931	22	1575.56	64.6075	23	1485.88	78.5403	24	1469.97	72.8793
25	1456.47	78.1889	26	1438.15	86.2776	27	1419.83	89.7092	28	1352.82	85.3081
29	1282.91	70.3815	30	1261.22	83.8411	31	1209.15	89.7827	32	1181.19	90.708
33	1138.28	74.8521	34	1105.98	75.2371	35	1059.21	85.6555	36	1024.5	88.0479
37	998.464	95.6655	38	966.162	89.7803	39	895.773	83.1269	40	865.4	84.8725
41	821.045	71.2085	42	803.669	85.0438	43	755.959	47.5122	44	737.156	66.0763
45	717.872	84.7556	46	705.337	83.8269	47	687.498	55.4633	48	636.394	91.6061



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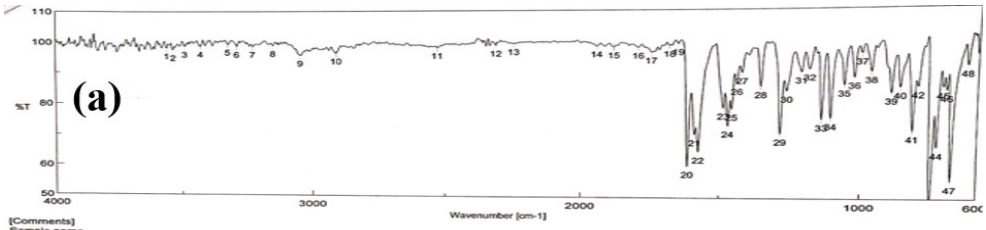
13	2571.61	99.1417	14	1916.9	98.6577	15	1791.55	88.0292	16	1657.52	51.4548
17	1611.23	67.977	18	1579.41	61.2667	19	1473.35	61.0192	20	1277.61	65.5696
21	1230.36	74.1804	22	1190.83	69.5322	23	1161.9	68.6222	24	1133.94	67.4265
25	1100.19	75.8496	26	1063.55	81.372	27	1026.91	83.6417	28	898.666	87.5053
29	836.955	85.26	30	740.531	55.397	31	691.355	58.9387			

Fig. S21 IR spectra of **L1** (a) and **L2** (b)



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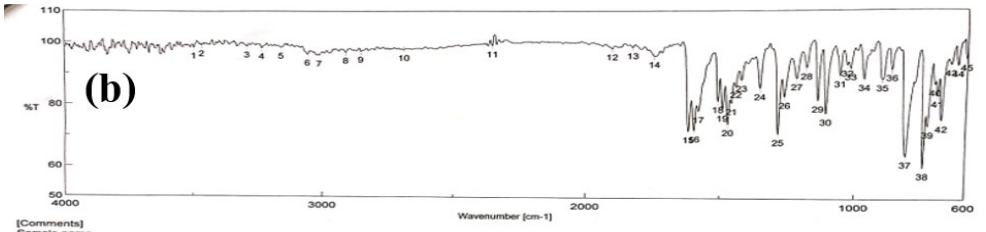
1	3567.66	97.8727	2	3542.59	97.3347	3	3498.72	98.4096	4	3437.01	98.4452
5	3332.39	99.1159	6	3297.68	98.3783	7	3237.41	98.3615	8	3158.83	98.6673
9	3054.21	95.4409	10	2917.77	96.1149	11	2536.42	97.8562	12	2318.02	98.6093
13	2252.45	99.1039	14	1946.31	98.3025	15	1884.11	97.9626	16	1794.92	97.8263
17	1747.19	96.2714	18	1681.14	98.4076	19	1649.32	98.9953	20	1614.61	60.042
21	1589.06	70.0931	22	1575.56	64.6075	23	1485.88	78.5403	24	1469.97	72.8793
25	1456.47	78.1889	26	1438.15	86.2778	27	1419.83	89.7092	28	1352.82	85.3081
29	1282.91	70.3815	30	1261.22	83.8411	31	1209.15	89.7827	32	1181.19	90.708
33	1138.28	74.8521	34	1105.98	75.2371	35	1059.21	85.6555	36	1024.5	88.0479
37	998.464	95.6655	38	966.162	89.7803	39	895.773	83.1269	40	865.4	84.8725
41	821.045	71.2085	42	803.689	85.0438	43	755.959	47.5122	44	737.156	66.0763
45	717.872	84.7556	46	705.337	83.8269	47	687.498	55.4633	48	636.394	91.6061



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User Amit Kumar Singh
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Company BHU

[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
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5	3166.06	98.1886	6	3064.33	95.9542	7	3018.53	95.6364	8	2916.32	96.6909
9	2858.95	96.8983	10	2692.62	97.3976	11	2357.07	98.5972	12	1904.84	97.7599
13	1826.74	98.1756	14	1746.23	95.3085	15	1617.02	71.3393	16	1595.81	71.5834
17	1579.9	77.7789	18	1507.58	80.9854	19	1490.22	78.276	20	1470.46	73.6545
21	1456.96	80.3348	22	1440.56	85.8079	23	1419.83	87.7263	24	1350.41	85.0398
25	1283.39	70.5406	26	1260.74	82.3371	27	1215.9	88.1584	28	1180.22	91.5746
29	1137.31	81.1399	30	1107.9	77.0172	31	1057.76	89.0849	32	1033.18	92.4577
33	1020.16	91.3262	34	970.019	87.897	35	904.451	87.7791	36	870.703	90.9804
37	815.259	63.5463	38	752.584	59.9065	39	738.603	72.9923	40	714.497	86.197
41	705.819	82.6802	42	688.945	74.8614	43	659.054	92.4184	44	633.019	92.1663
45	602.646	94.1399									

Fig. S22 IR spectra of **C1** (a) and **C2** (b).

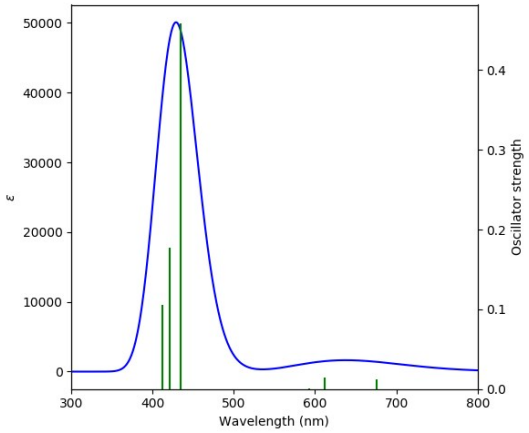

Fig. S23 UV-vis spectra of **C1** obtained from TD-DFT calculations.

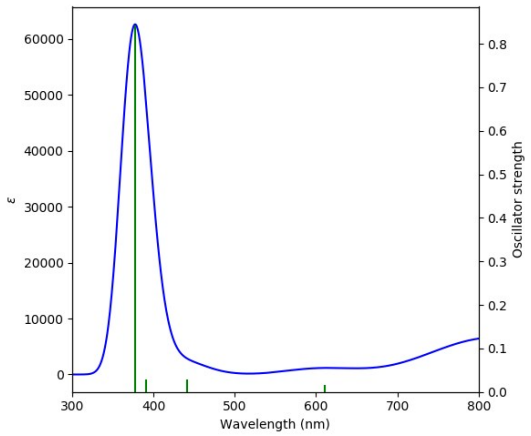

Fig. S24 UV−vis spectra of **C2** obtained from TD-DFT calculations.

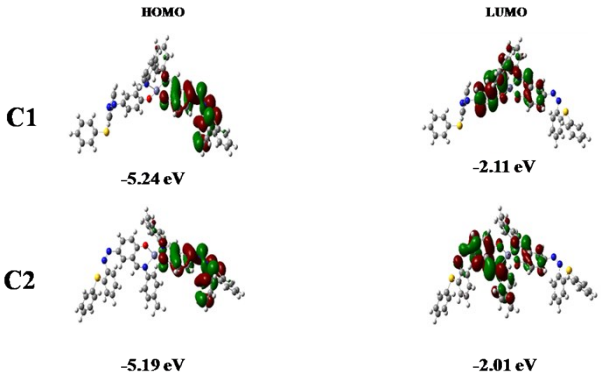

Fig. S25 Frontier molecular orbitals of complexes *cis*–**C1** and *cis*–**C2** obtained from the DFT calculations.

Table S1. Selected crystallographic parameter for **C1** and **C2**

C1	**Bond Length (Å)**	**C2**	**Bond Length (Å)**
Zn1 – O2	1.920(2)	C6 – S1	1.771(3)
Zn1 – O1	1.907(2)	S1 – C8	1.780(3)
Zn1 – N3	2.012(3)	N3 – C13	1.425(3)
Zn1 – N4	1.999(3)	N2 – N1	1.266(3)
S2 – C43	1.767(4)	C16 – N2	1.419(3)
S2 – C44	1.782(4)	C19 – O1	1.302(3)
S1 – C7	1.771(4)	C22 – N3	1.306(3)
O2 – C33	1.295(4)	Zn1 – N3	1.996(2)
O1 – C16	1.298(4)	N3 – C26	1.418(3)
N3 – C19	1.288(4)	Zn1 – O1	1.918(2)
N3 – C20	1.434(4)	Zn1 – O2	1.918(2)
N4 – C31	1.294(4)	Zn1 – N4	2.007(2)
N2 – N1	1.275(4)	O2 – C34	1.307(3)
N2 – C13	1.410(4)	C37 – N5	1.422(3)
N5 – N6	1.244(4)	C40 – N4	1.298(3)
N6 – C38	1.434(4)	N4 – C42	1.431(3)
N5 – C36	1.421(4)	N5 – N6	1.249(3)
N1 – C12	1.426(4)	N6 – C51	1.514(4)

C1	**Bond Angle (°)**	**C2**	**Bond Angle (°)**
O1 Zn1 O2	111.47(1)	C8 S1 C6	101.57(1)
N3 Zn1 O2	125.55(1)	N2 N1 C13	114.1(2)
N3 Zn1 O1	95.95(1)	N1 C13 C8	115.7(2)
N4 Zn1 O2	97.66(1)	N1 C13 C12	124.6(2)

N4 Zn1 O1	128.00(1)	C16 N2 N1	113.3(2)
N4 Zn1 N3	103.46(1)	O1 C19 C18	118.8(2)
C44 S2 C43	104.24(1)	O1 C19 C20	123.7(2)
C33 O2 Zn1	124.3(2)	Zn1 N3 C22	119.86(2)
C19 N3 Zn1	121.8(2)	C26 N3 C22	119.8(2)
C20 N3 Zn1	119.0(2)	C26 N3 Zn1	120.04(2)
C20 N3 C19	118.9(5)	Zn1 O1 C19	125.43(17)
C31 N4 Zn1	121.0(2)	O1 Zn1 N3	97.20(8)
C25 N4 Zn1	121.0(2)	O2 Zn1 N3	123.48(8)
C25 N4 C31	118.8(3)	O2 Zn1 O1	111.18(9)
C13 N2 N1	114.7(3)	N4 Zn1 N3	111.52(9)
C38 N6 N5	112.1(3)	N4 Zn1 O1	118.95(8)
C36 N5 N6	115.4(3)	N4 Zn1 O2	96.23(8)
C12 N1 N2	112.5(3)	C40 N4 Zn1	119.88(2)
C17 C16 O1	117.8(3)	C42 N4 Zn1	120.84(1)