CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

DOI:10.1002/chem. 200801396

Supplementary Materials For

Attachment of Different Donor Groups to a Cryptand for Modulation of Two-Photon Absorption Cross-Section

Atanu Jana[a], So Young Jang[b], Jae-Yoon Shin[b], Arijit Kumar De[a], Debabrata Goswami[a], Dongho Kim*[b] and Parimal K. Bharadwaj*[a]

[a] A. Jana, A. K. De, Dr. D. Goswami, Prof. Dr. P. K. Bharadwaj
Department of Chemistry, Indian Institute of Technology Kanpur
Kanpur 208016 (India)
Fax: (+91)512-259-7436
Email: pkb@iitk.ac.in

[b] S. Y. Jang, J.-Y. Shin, Prof. Dr. D. Kim
Department of Chemistry, Yonsei University
Seoul 120749 (Korea)
Fax: (+82)2-2123-2434
Email: dongho@yonsei.ac.kr

Legends for the Scheme and Figures

Scheme 1. Donor−Acceptor models for cryptand based TPA active molecules.

Section 1: Experimental Section.

Fig. S1–S2: 400MHz ^{1}H NMR spectrum and ^{13}C NMR spectrum of $\mathbf{L_4}$.

Fig. S3–S4: ESI-MS spectra of $\mathbf{L_4}$ and 400MHz ^{1}H NMR spectrum of $\mathbf{L_5}$.

Fig. S5–S6: ^{13}C NMR spectrum of $\mathbf{L_5}$ and ESI-MS spectra of $\mathbf{L_5}$.

Fig. S7–S8: 400MHz ^{1}H NMR spectrum and ^{13}C NMR spectrum of $\mathbf{L_6}$.

Fig. S9–S10: ESI-MS spectra of $\mathbf{L_6}$ and 400MHz ^{1}H NMR spectrum of $\mathbf{L_7}$.

Fig. S11–S12: ^{13}C NMR spectrum of $\mathbf{L_7}$ and FAB-MS spectra of $\mathbf{L_7}$.

Figure S13–S14: 400MHz ^{1}H NMR spectrum and ^{13}C NMR spectrum of $\mathbf{L_8}$.

Section 2: UV-vis spectra.

Fig.S34: Absorption spectra of all the chromophores with Cd^{II} perchlorate in 10^{-5}(M) CH_3CN.

Fig.S35: (a) Absorption spectra of the chromophore $\mathbf{L_7}$ as a function of $[Zn^{II}]$. The arrows indicate the trend for increasing $[Zn^{II}]$. The $[\mathbf{L_7}]$ is 1×10^{-5} (M). (b) Plot of $A_0/A-A_0$ against $[Zn^{II}]^{-1}$ for binding constant determination.

Fig.S36: (a) Absorption spectra of the chromophore $\mathbf{L_8}$ as a function of $[Zn^{II}]$. The arrows indicate the trend for increasing $[Zn^{II}]$. The $[\mathbf{L_8}]$ is 1×10^{-5} (M). (b) Plot of $A_0/A-A_0$ against $[Zn^{II}]^{-1}$ for binding constant determination.

Fig.S37: (a) Absorption spectra of the chromophore $\mathbf{L_9}$ as a function of $[Zn^{II}]$. The arrows indicate the trend for increasing $[Zn^{II}]$. The $[\mathbf{L_9}]$ is 1×10^{-5} (M). (b) Plot of $A_0/A-A_0$ against $[Zn^{II}]^{-1}$ for binding constant determination.

Table 3: Atomic numbers and the optimized X, Y, Z Cartesian coordinates for **L_8** in Å unit.

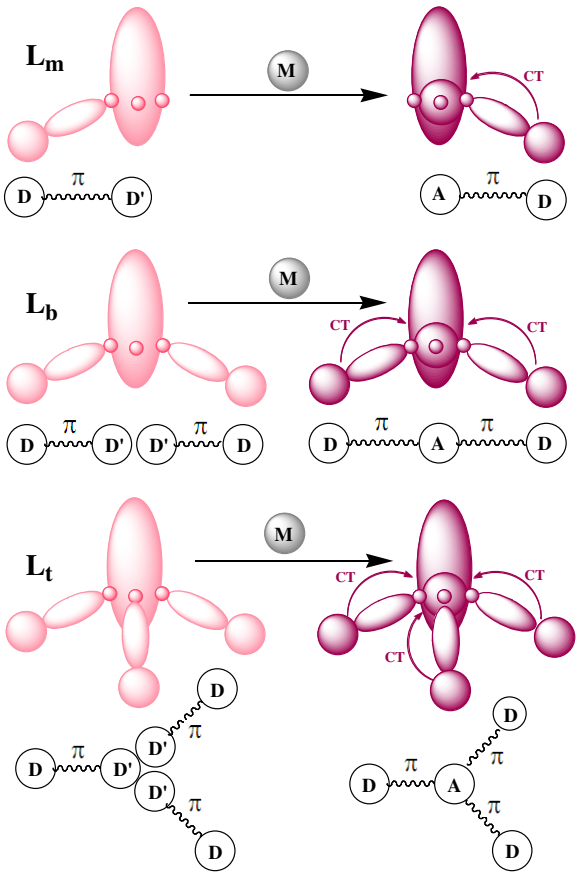
Table 4: Atomic numbers and the optimized X, Y, Z Cartesian coordinates for Zn^{II} complex of ligand **L_8** in Å unit.

Table 5: Atomic numbers and the optimized X, Y, Z Cartesian coordinates for **L_9** in Å unit.

Table 6: Atomic numbers and the optimized X, Y, Z Cartesian coordinates for Zn^{II} complex of **L_9** in Å unit.

Fig. S44: Contour surfaces of HOMO−1, HOMO, LUMO and LUMO+1 for all the ligands and their corresponding Zn^{II} complexes.

References.



Scheme 1

Section 1: Experimental Section.

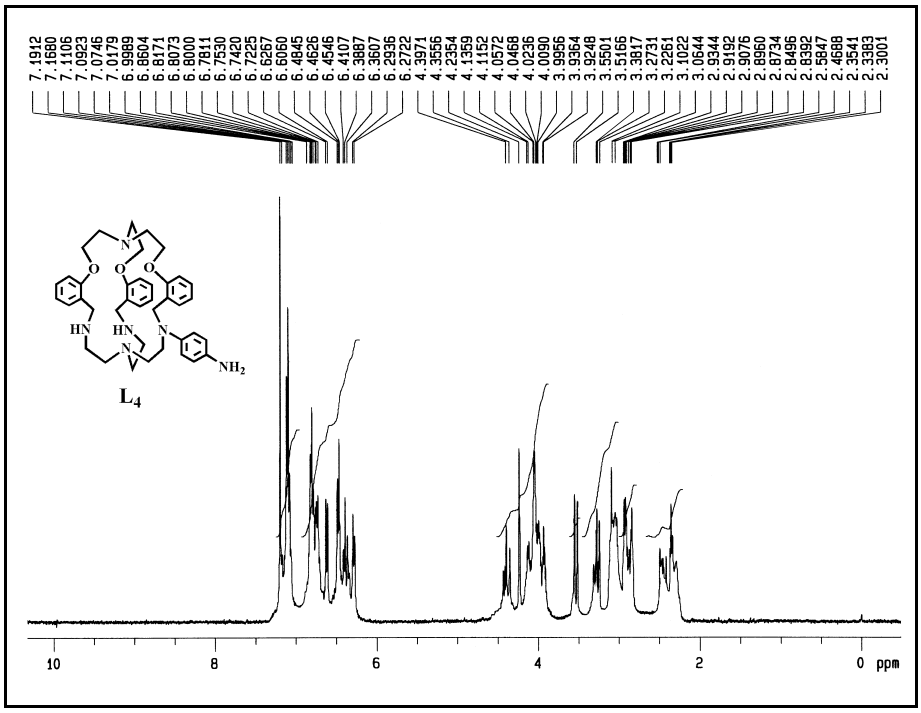


***Figure S1**:* 400 MHz ^{1}H NMR spectra of ligand $\mathbf{L_4}$

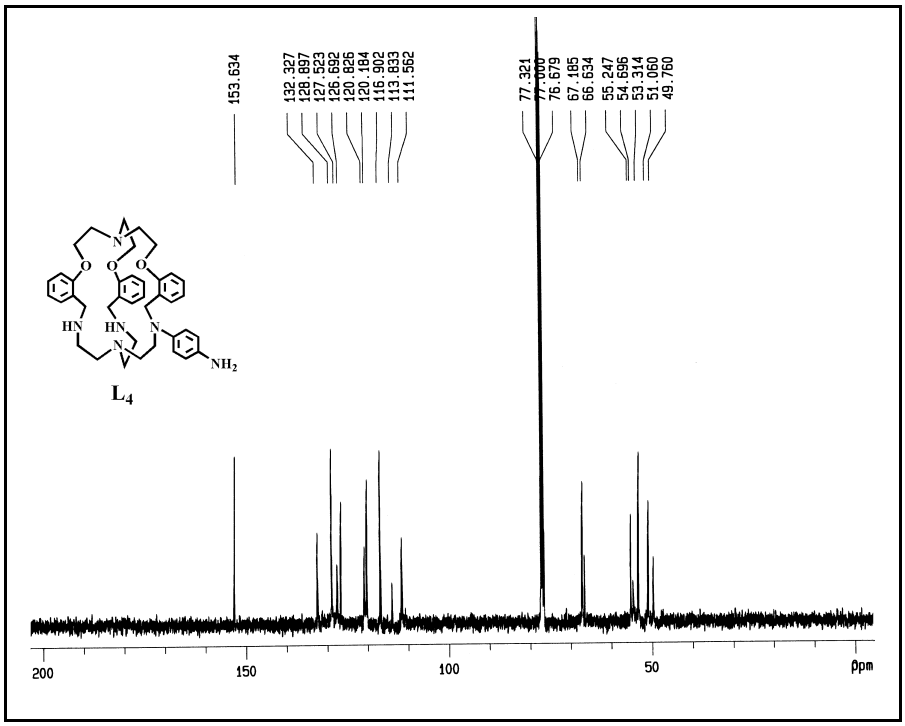


***Figure S2**:* ^{13}C NMR spectra of ligand $\mathbf{L_4}$

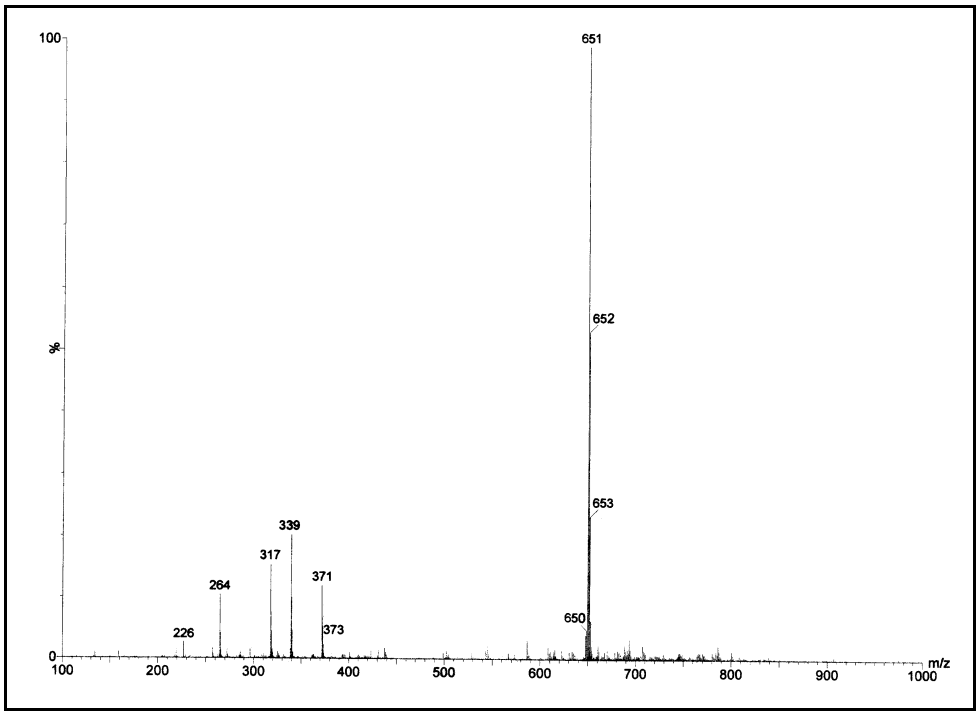


Figure S3: ESI-MS spectra of ligand $\mathbf{L_4}$

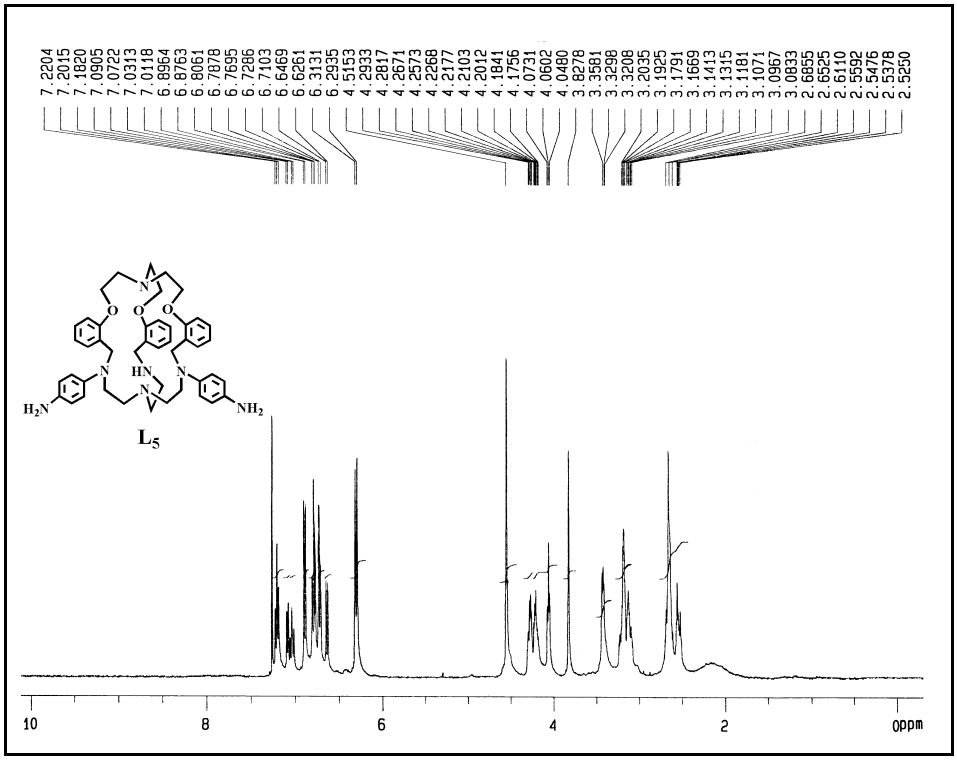


Figure S4: 400 MHz ^{1}H NMR spectra of ligand $\mathbf{L_5}$

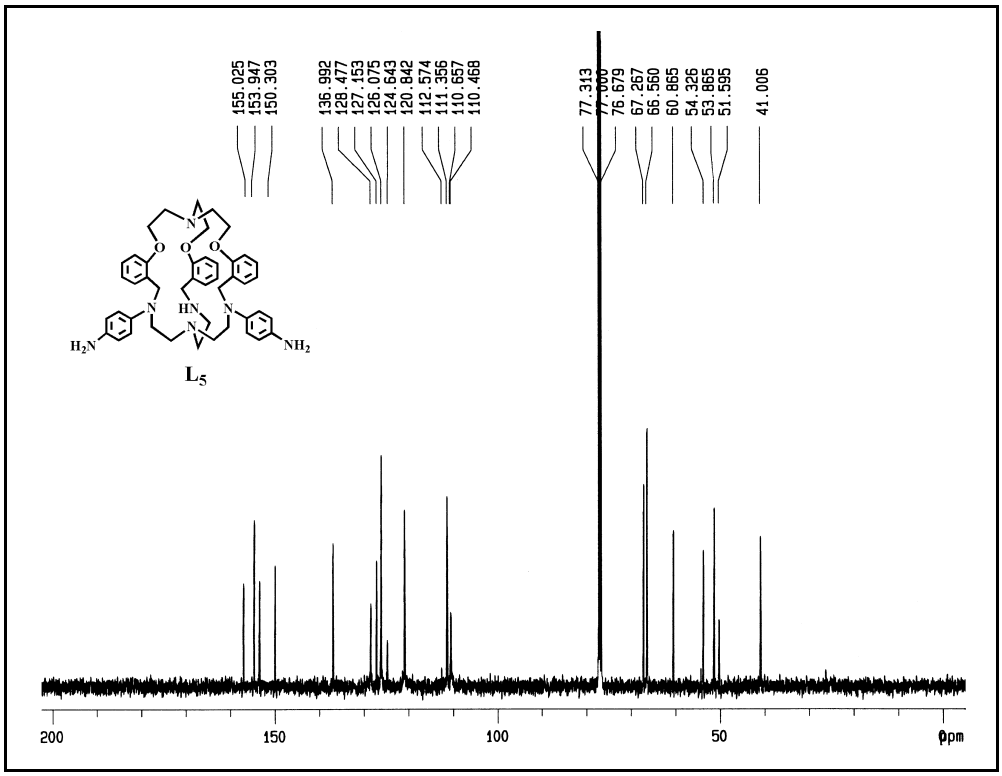


***Figure S5**:* ^{13}C NMR spectra of ligand $\mathbf{L_5}$

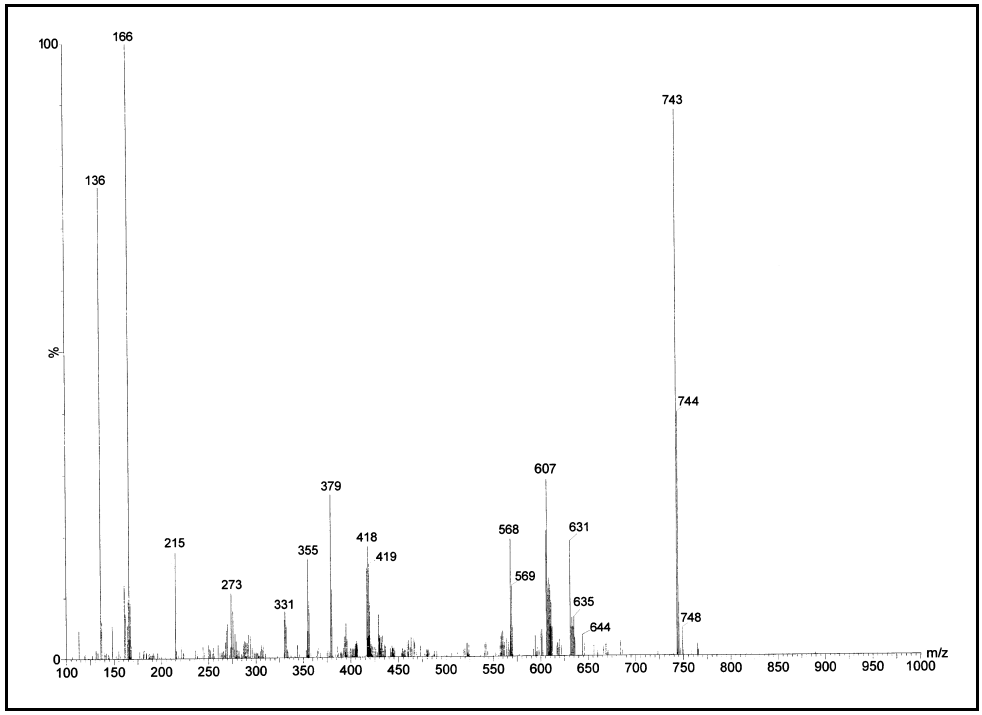


***Figure S6**:* ESI-MS spectra of ligand $\mathbf{L_5}$

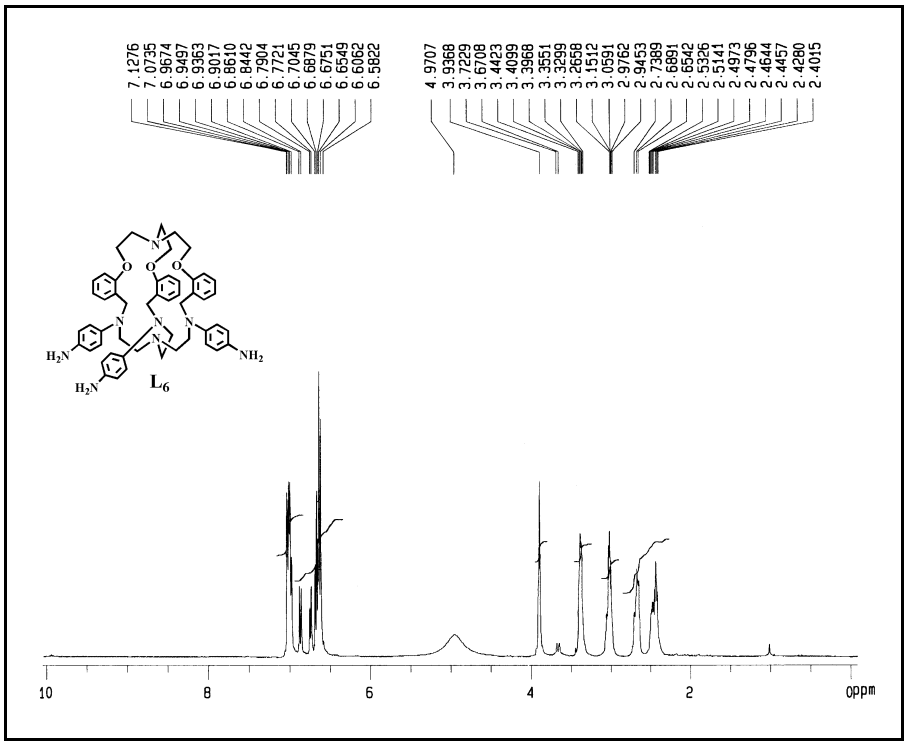


Figure S7: 400 MHz ^{1}H NMR spectra of ligand $\mathbf{L_6}$

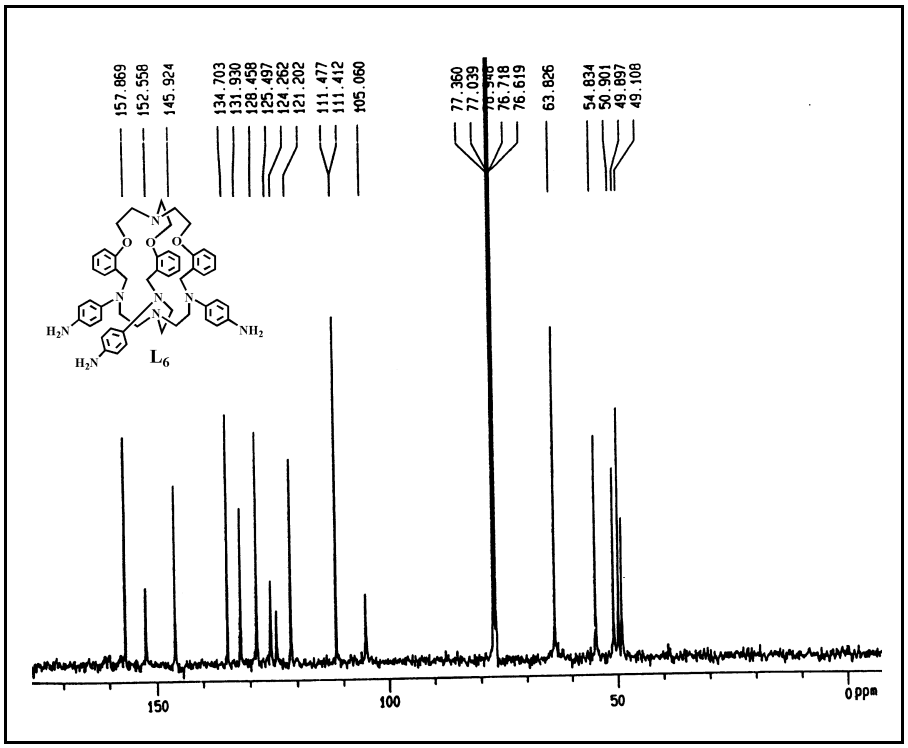


Figure S8: ^{13}C NMR spectra of ligand $\mathbf{L_6}$

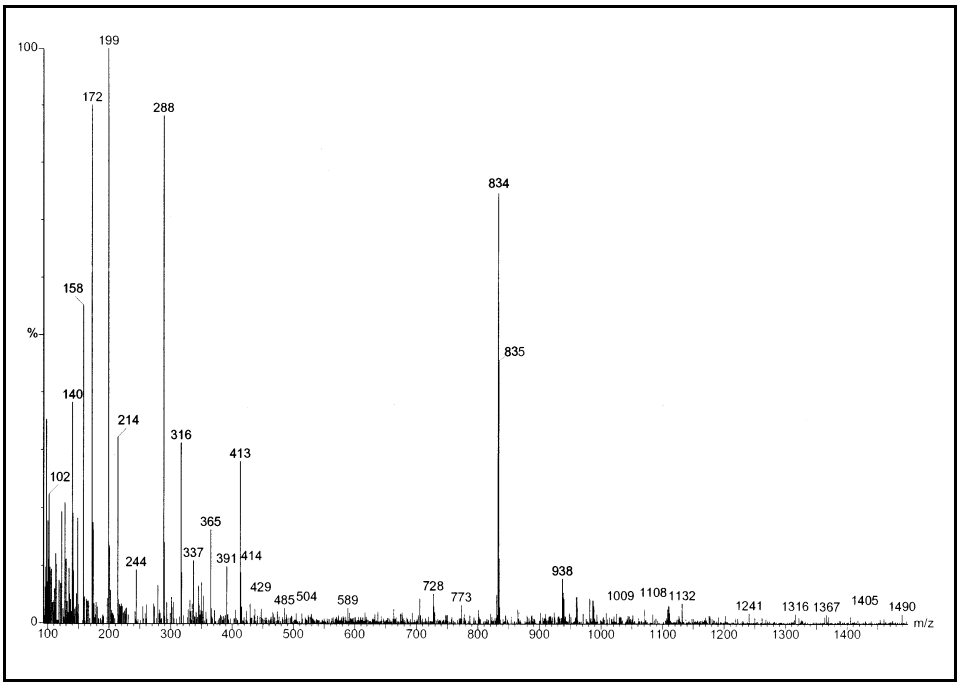


***Figure S9**:* ESI-MS spectra of ligand $\mathbf{L_6}$

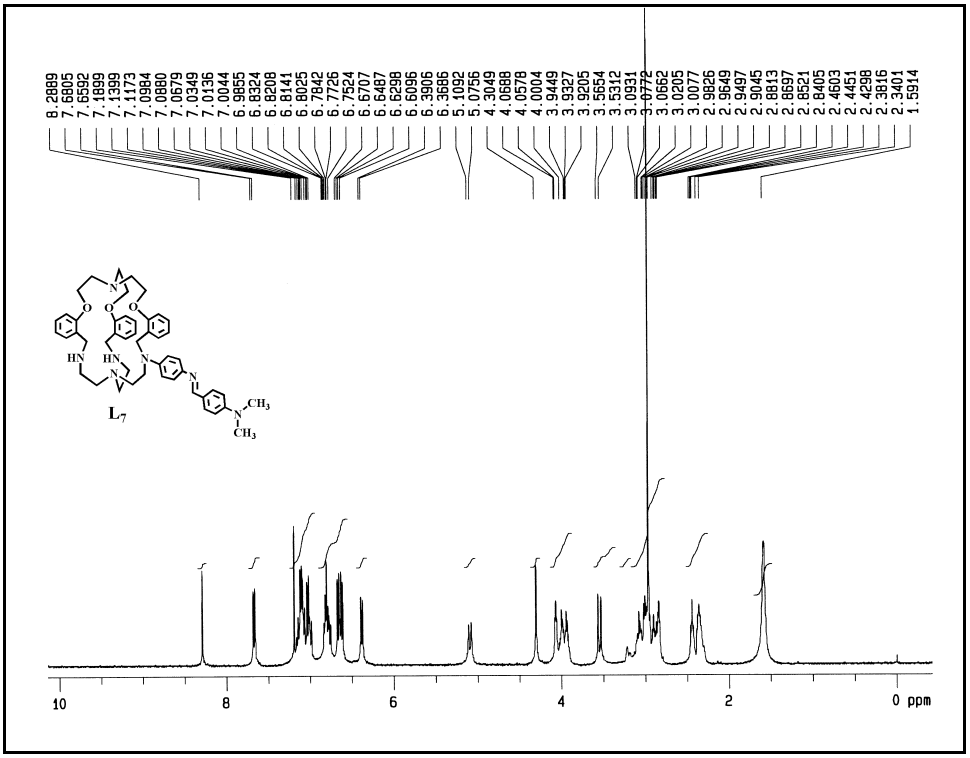


***Figure S10**:* 400 MHz ^{1}H NMR spectra of ligand $\mathbf{L_7}$

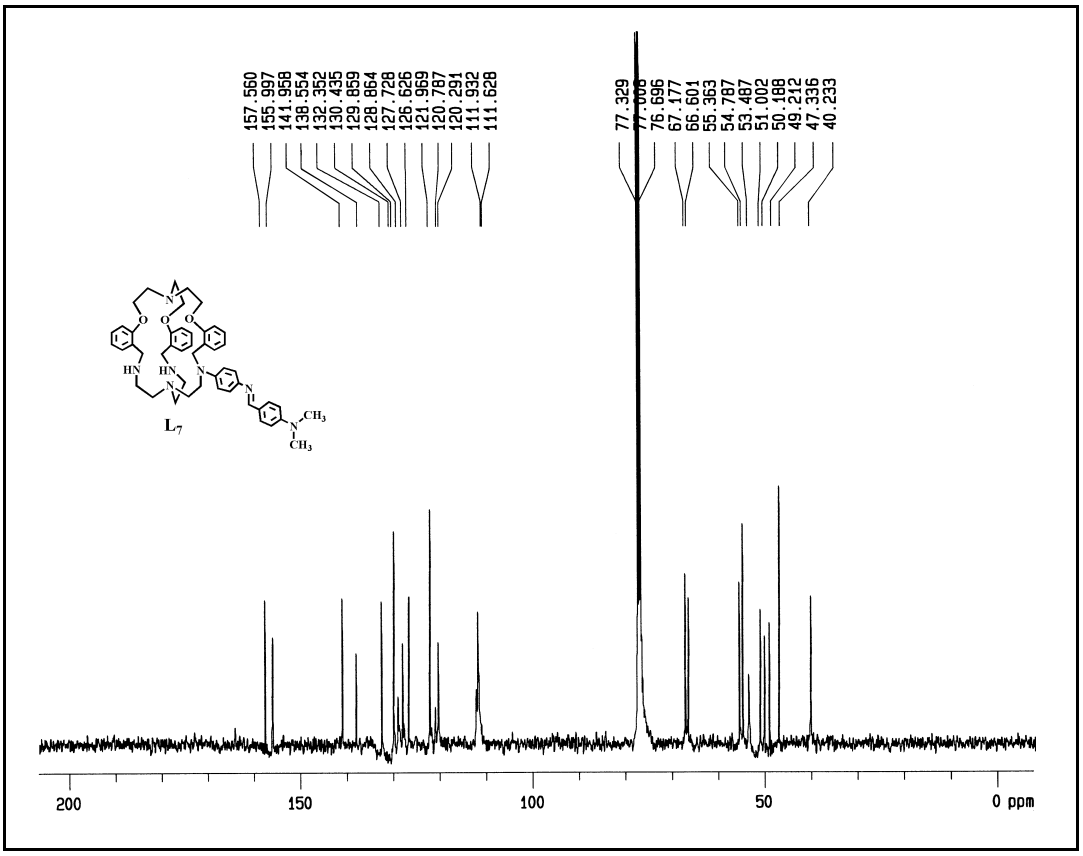


Figure S11: ^{13}C NMR spectra of ligand $\mathbf{L_7}$

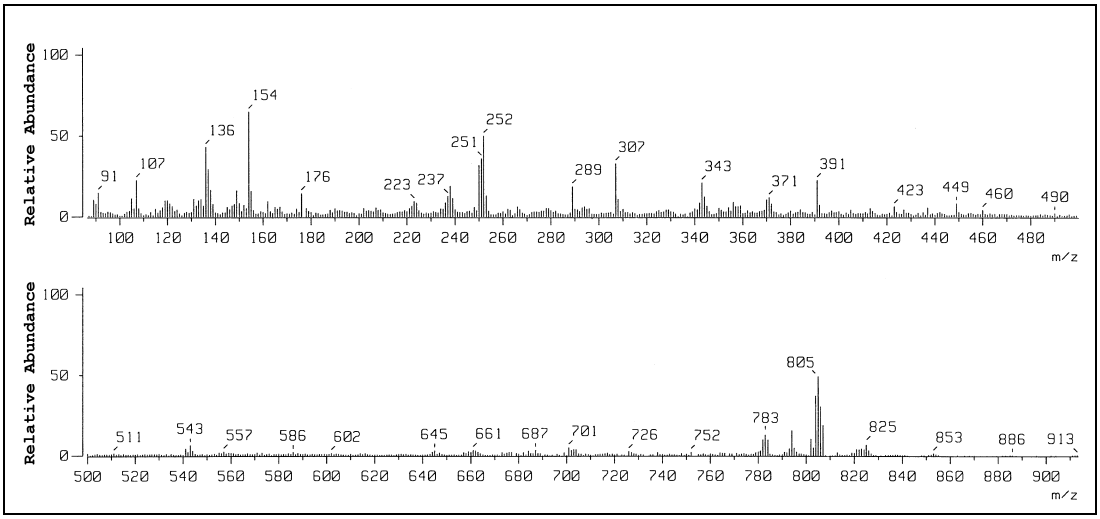


Figure S12: FAB-MS spectra of Schiff Base $\mathbf{L_7}$

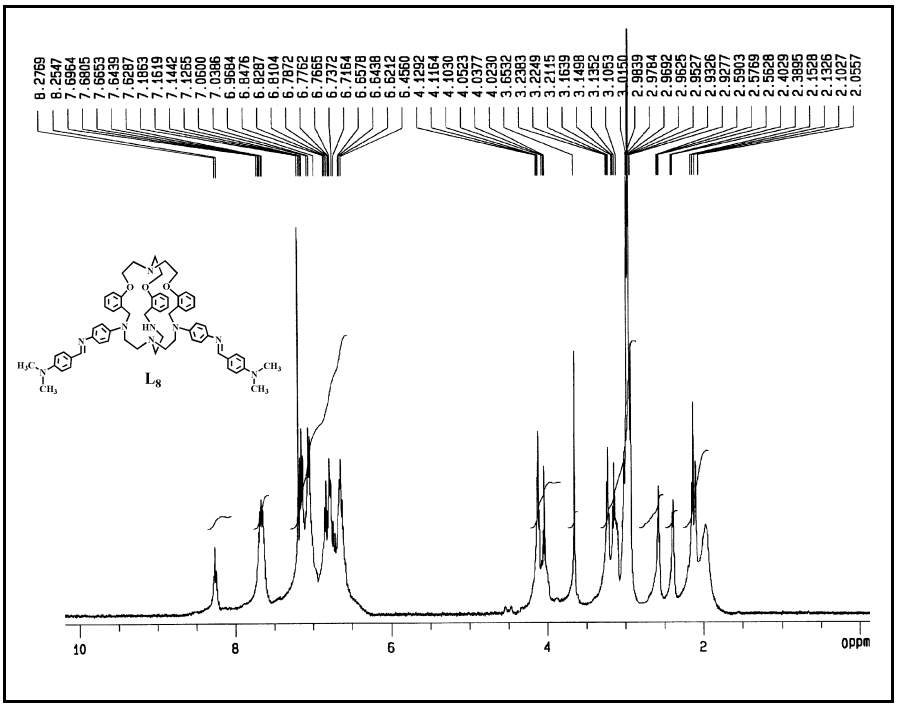


***Figure S13**:* 400 MHz ^{1}H NMR spectra of ligand $\mathbf{L_8}$

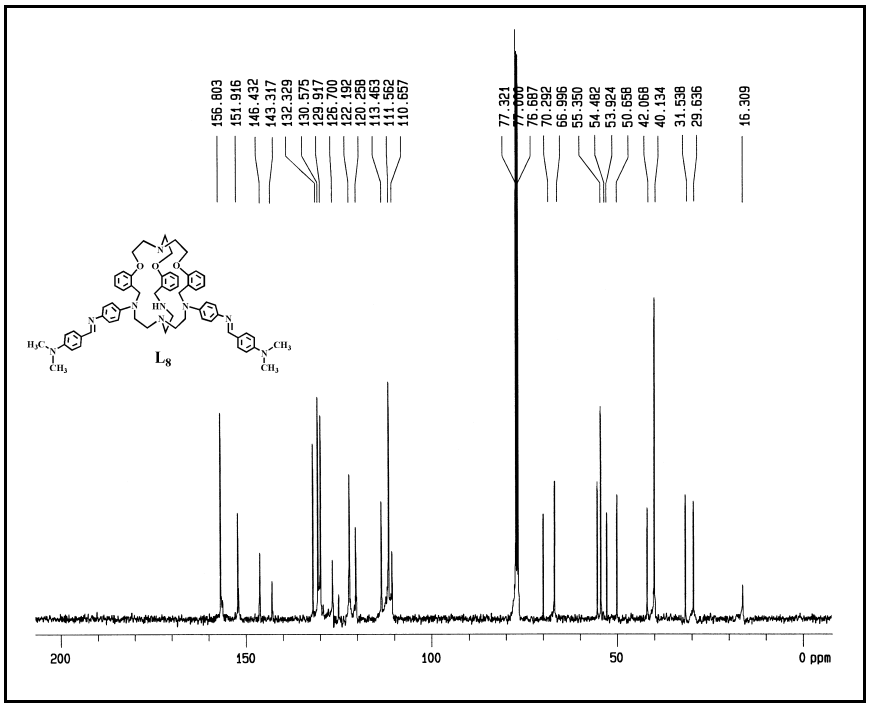


***Figure S14**:* ^{13}C NMR spectra of ligand $\mathbf{L_8}$

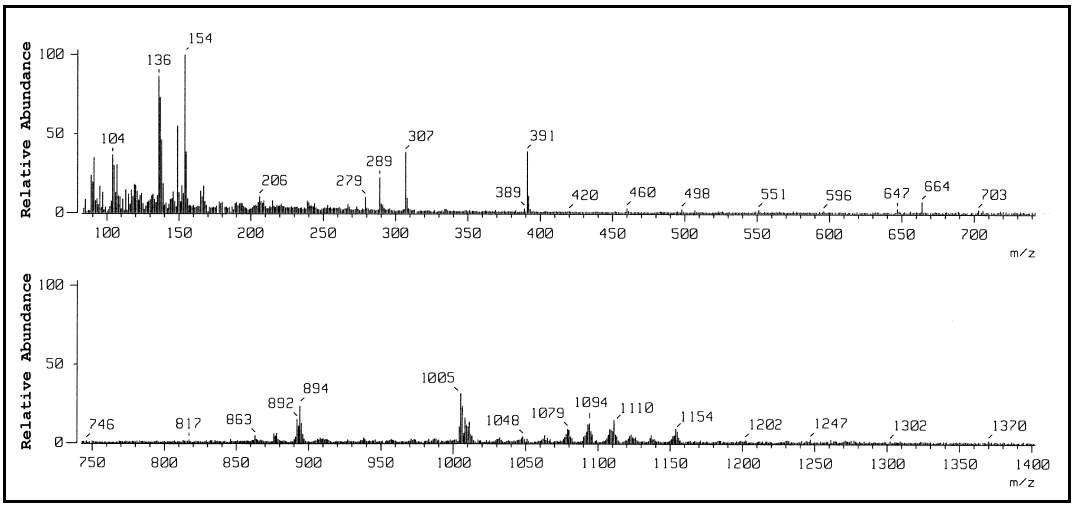


Figure S15: FAB-MS spectra of Schiff Base $\mathbf{L_8}$

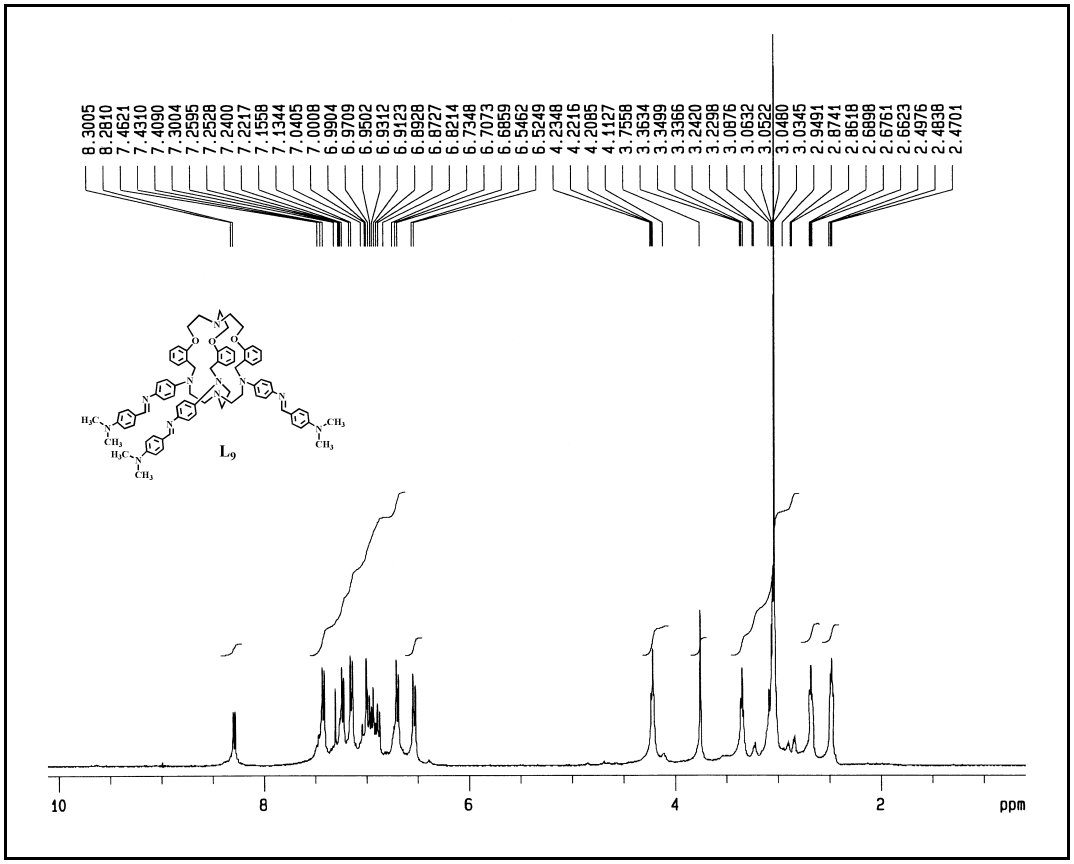


Figure S16: ^{1}H NMR spectra of ligands $\mathbf{L_9}$

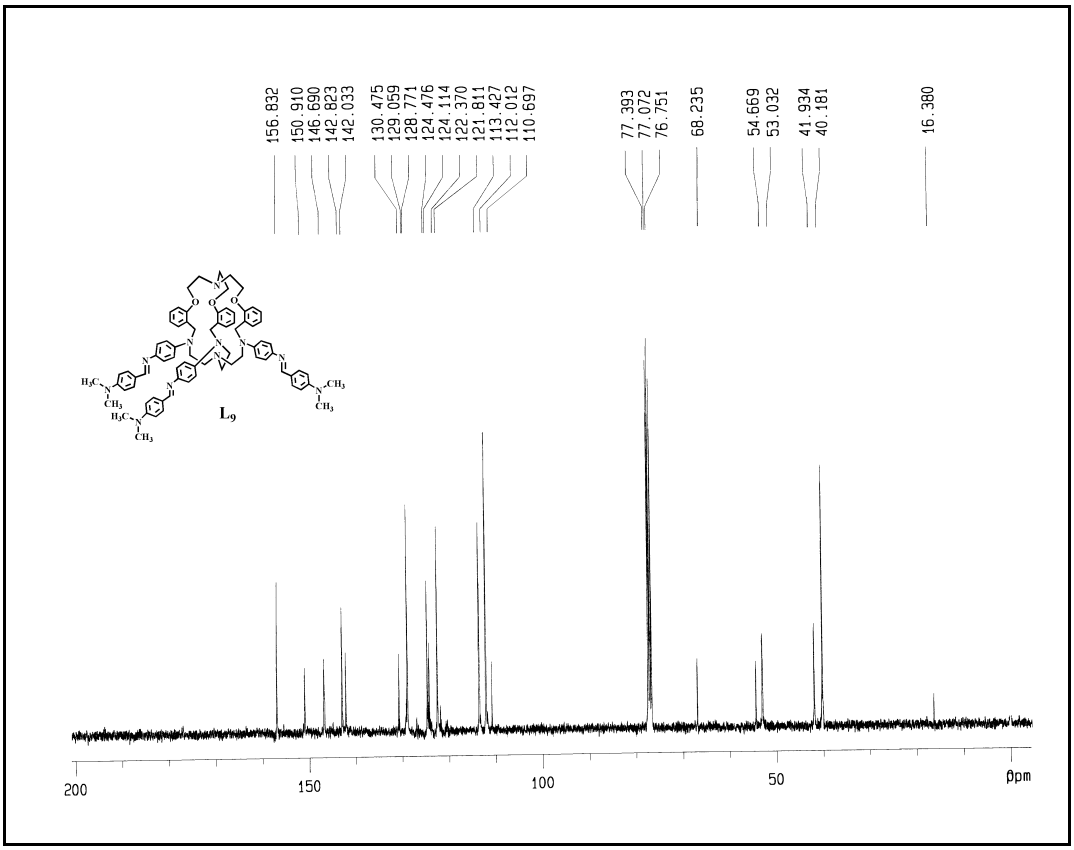


Figure S17: ^{13}C NMR spectra of ligand **L_9**

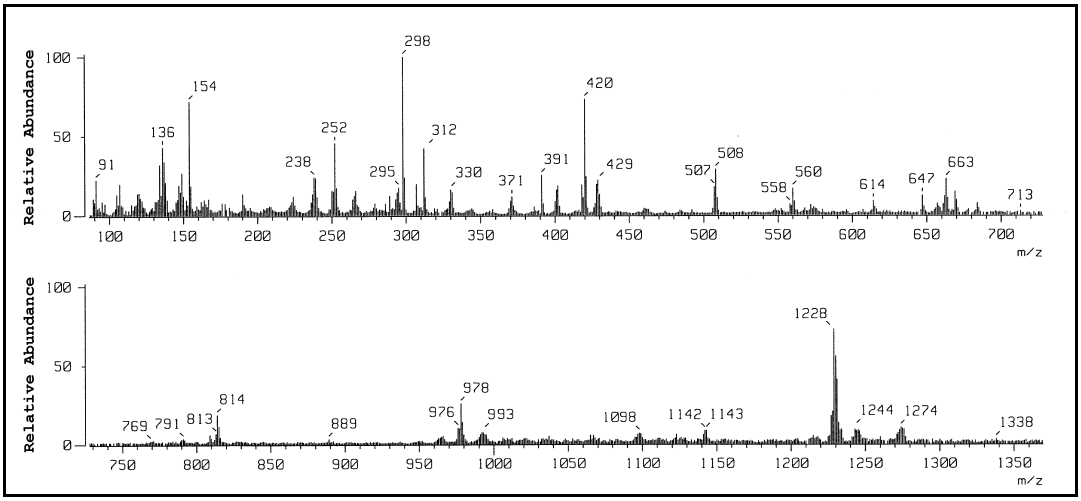


Figure S18: FAB-MS spectra of Schiff Base **L_9**

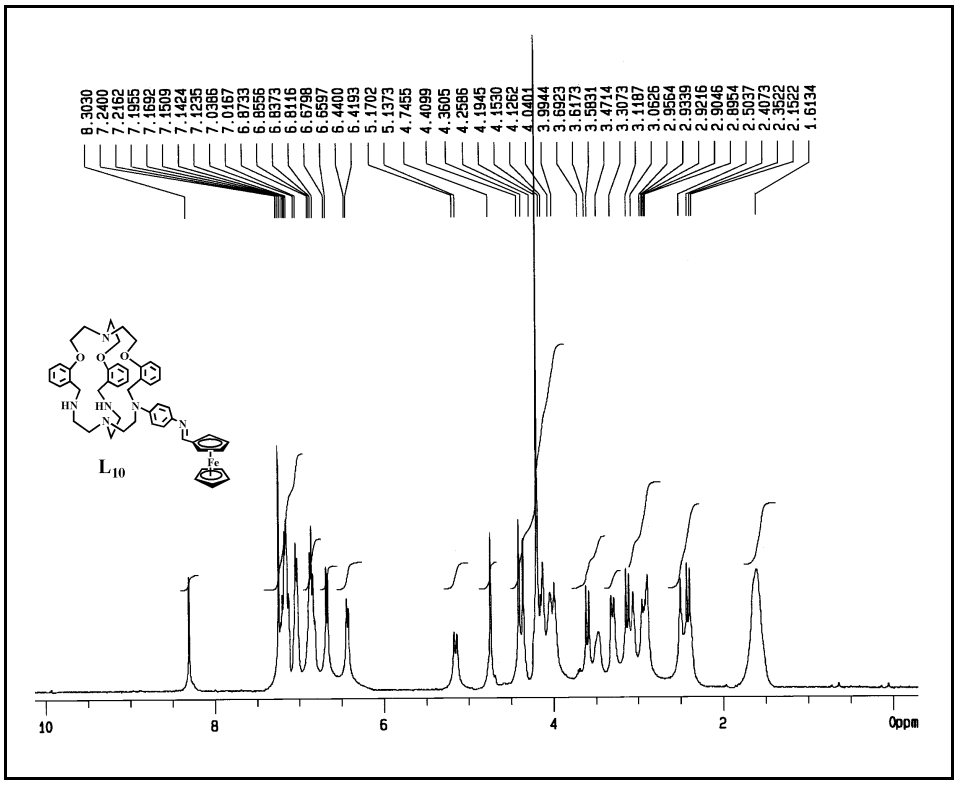


Figure S19: 400 MHz ^{1}H NMR spectra of ligand $\mathbf{L_{10}}$

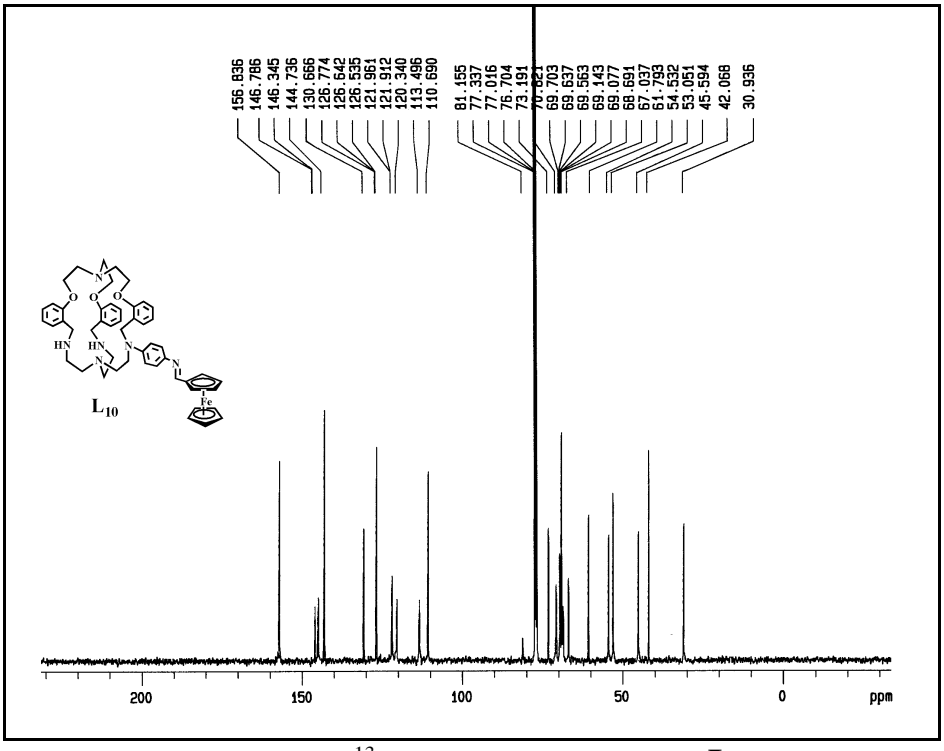


Figure S20: ^{13}C NMR spectra of ligand $\mathbf{L_{10}}$

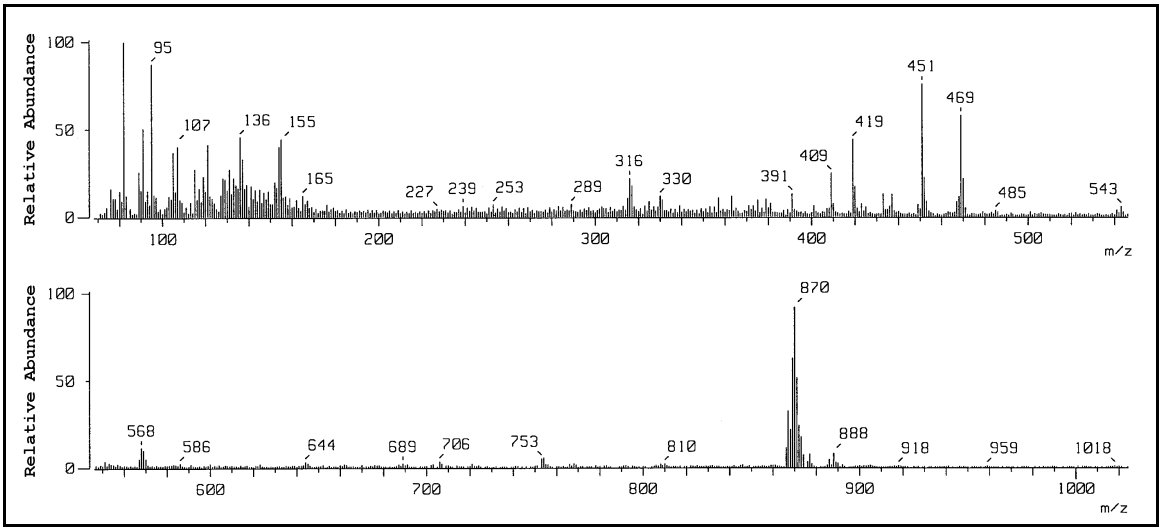


Figure S21: FAB-MS spectra of Schiff Base $\mathbf{L_{10}}$

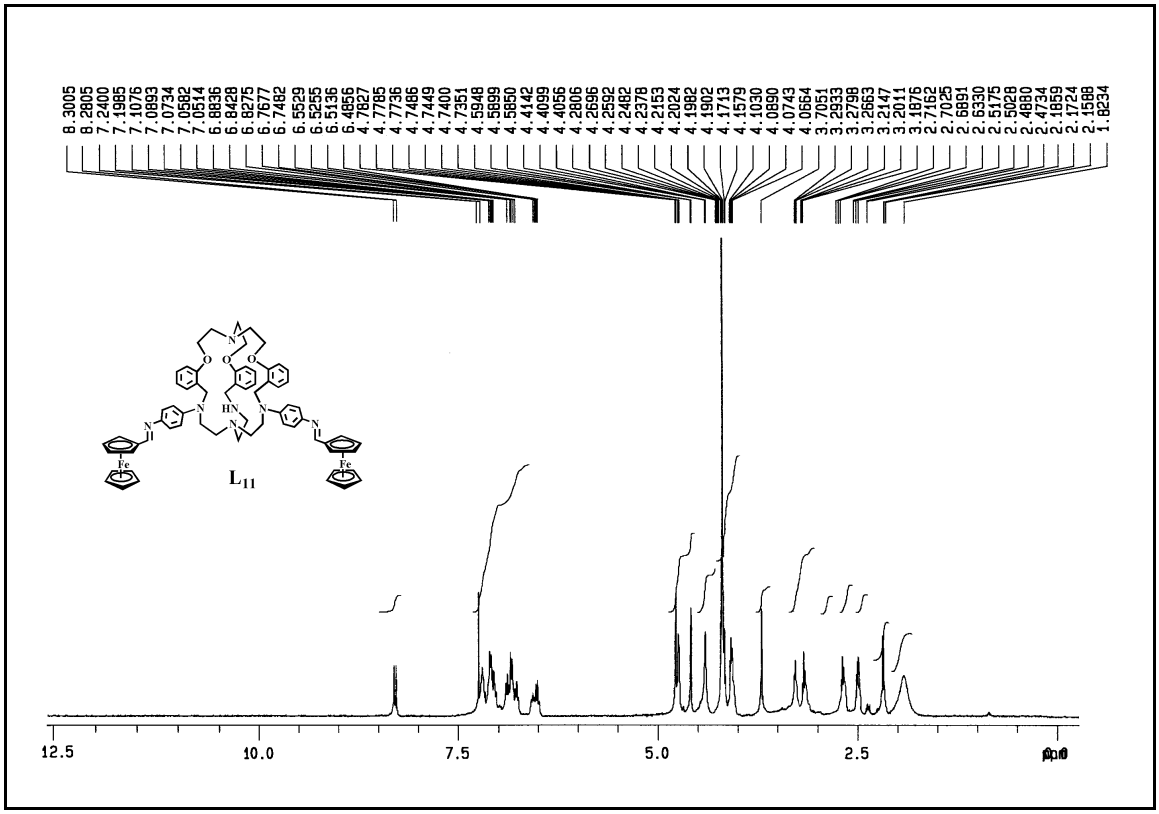


Figure S22*:* 400 MHz ^{1}H NMR spectra of ligands $\mathbf{L_{11}}$

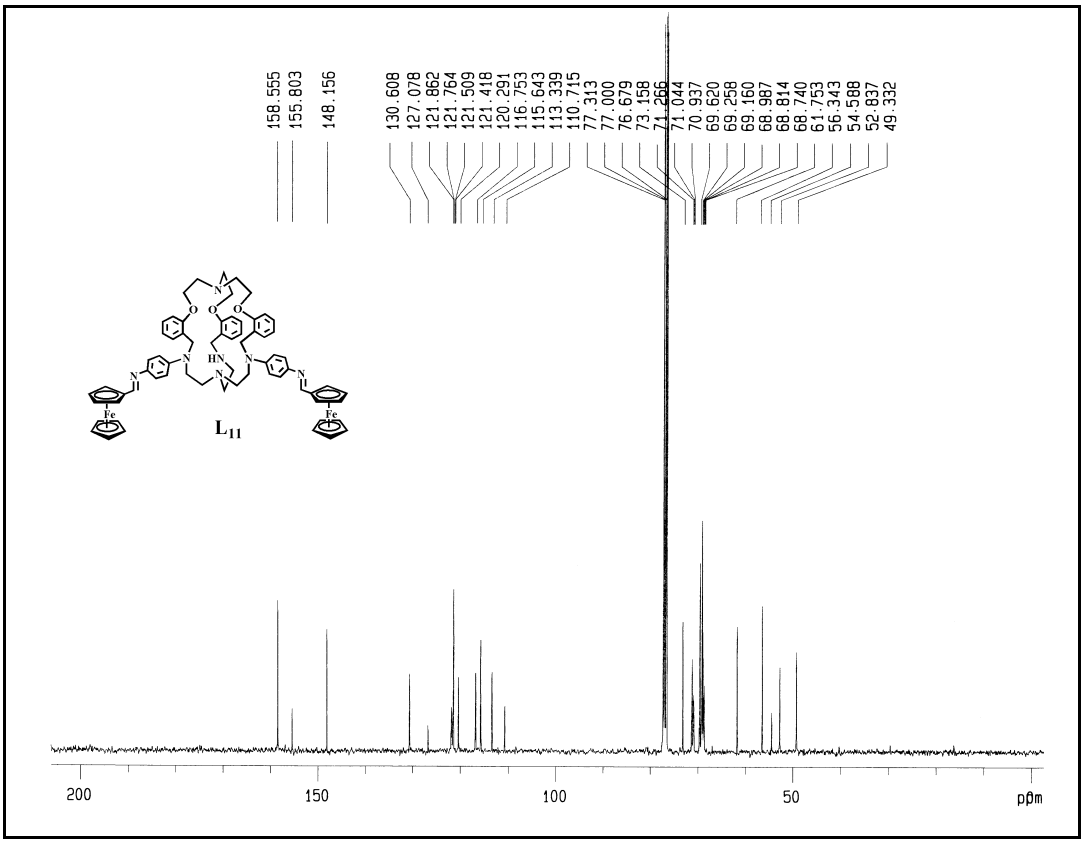


Figure S23: ^{13}C NMR spectra of ligand $\mathbf{L_{11}}$

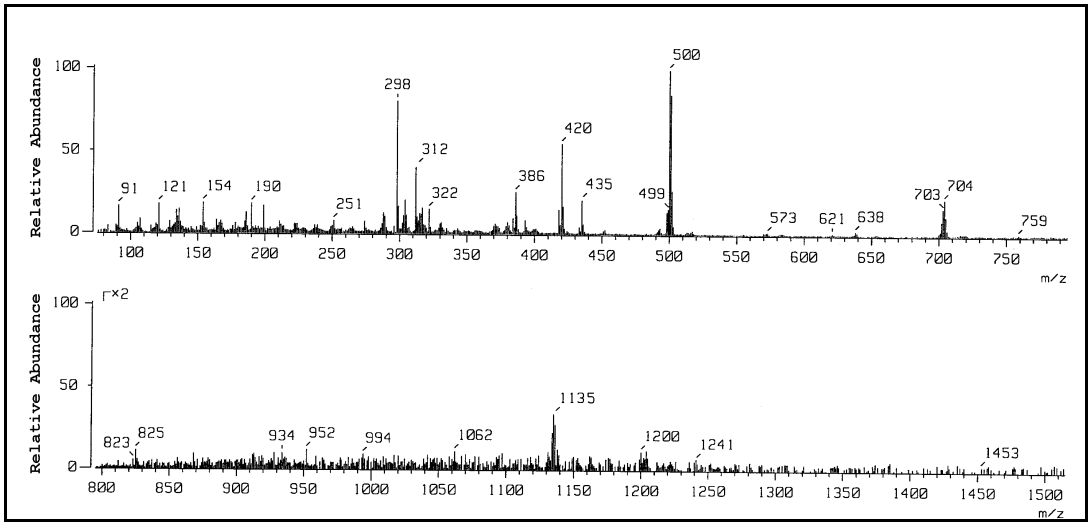


Figure S24: FAB-MS spectra of Schiff Base $\mathbf{L_{11}}$

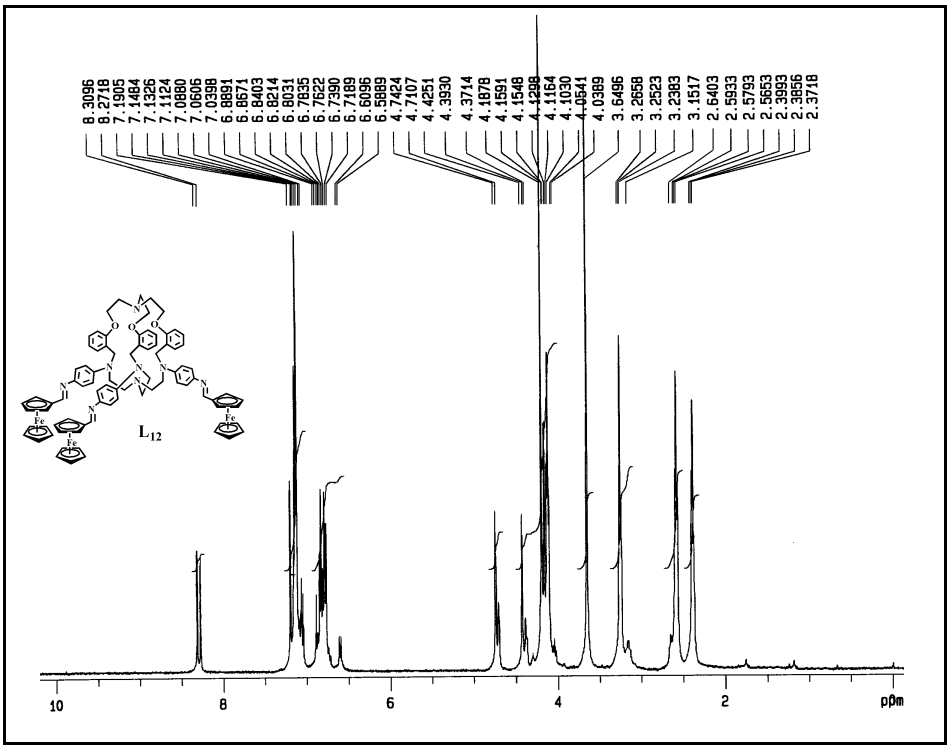


Figure S25: 400 MHz ^{1}H NMR spectra of ligand $\mathbf{L_{12}}$

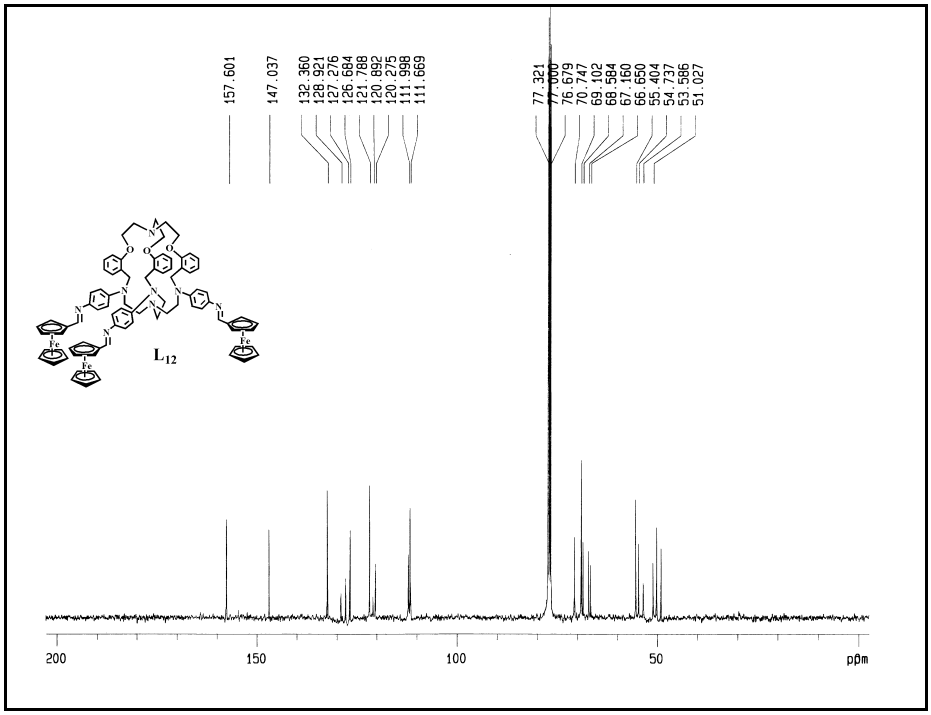


Figure S26: ^{13}C NMR spectra of ligand $\mathbf{L_{12}}$

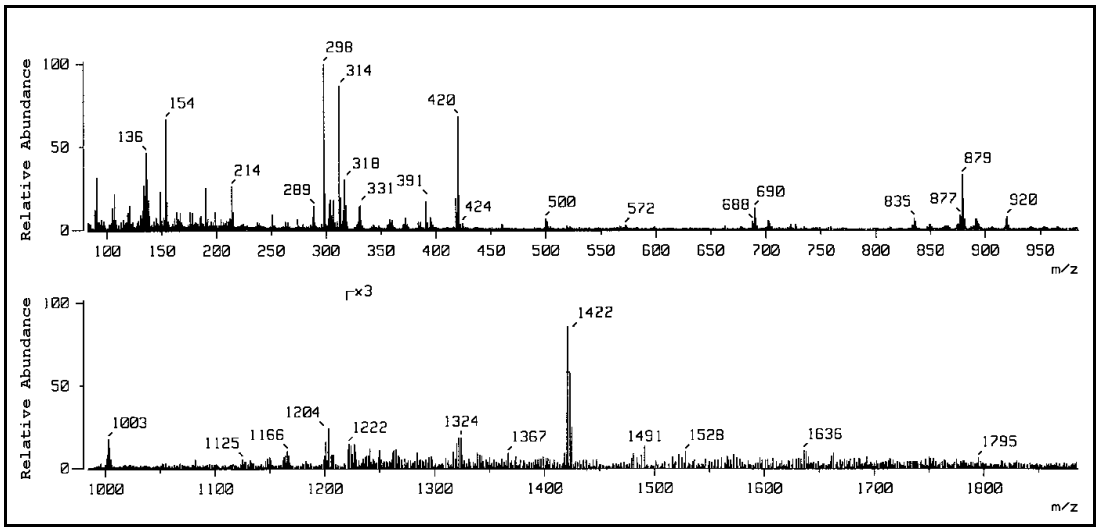


Figure S27: FAB-MS spectra of Schiff Base $\mathbf{L_{12}}$

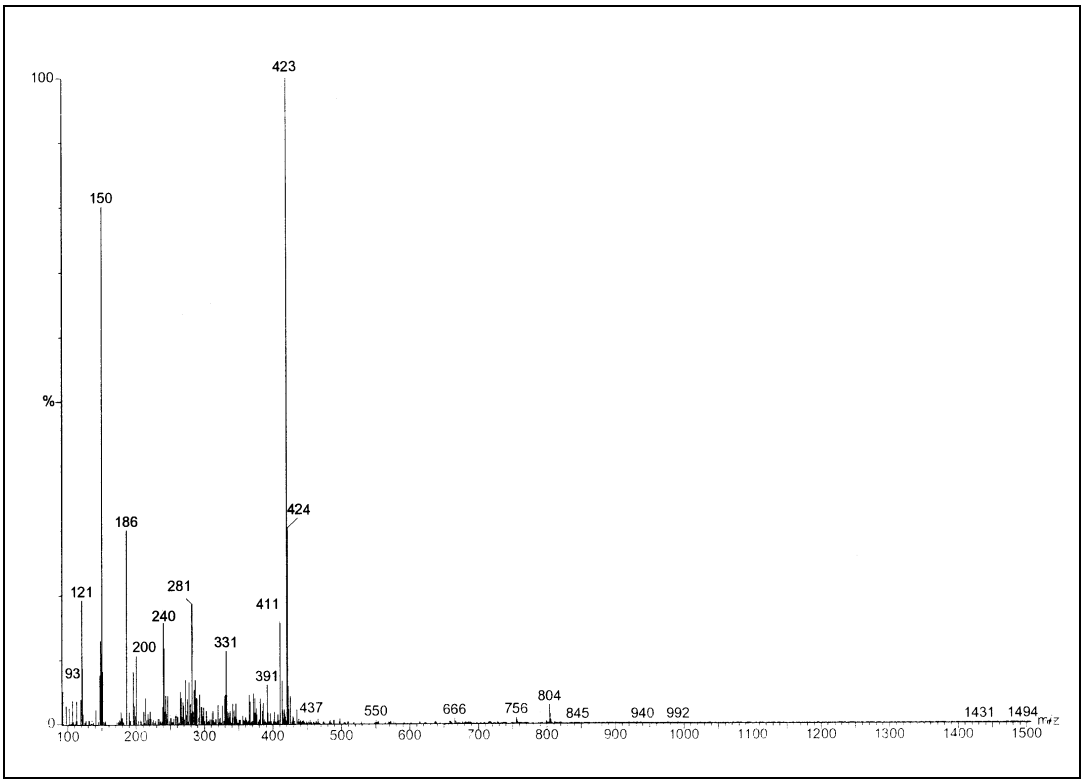


Figure S28: ESI-MS spectra of Zn^{II} complex of $\mathbf{L_7}$

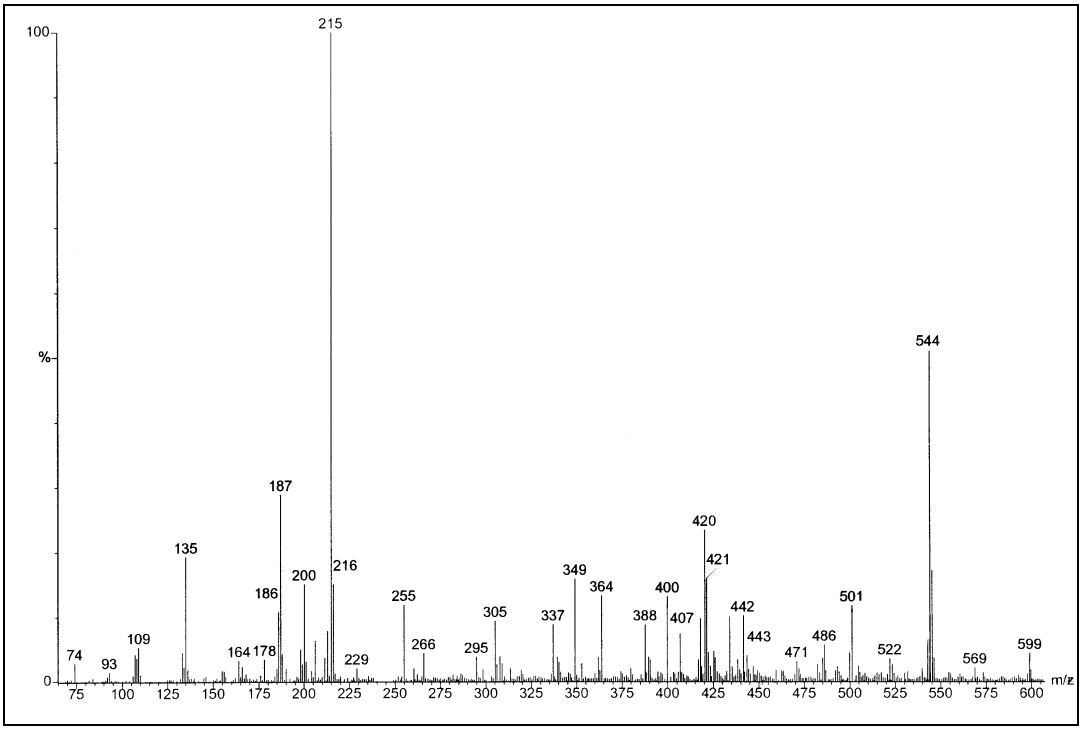


Figure S29: ESI-MS spectra of Zn^{II} complex of $\mathbf{L_8}$

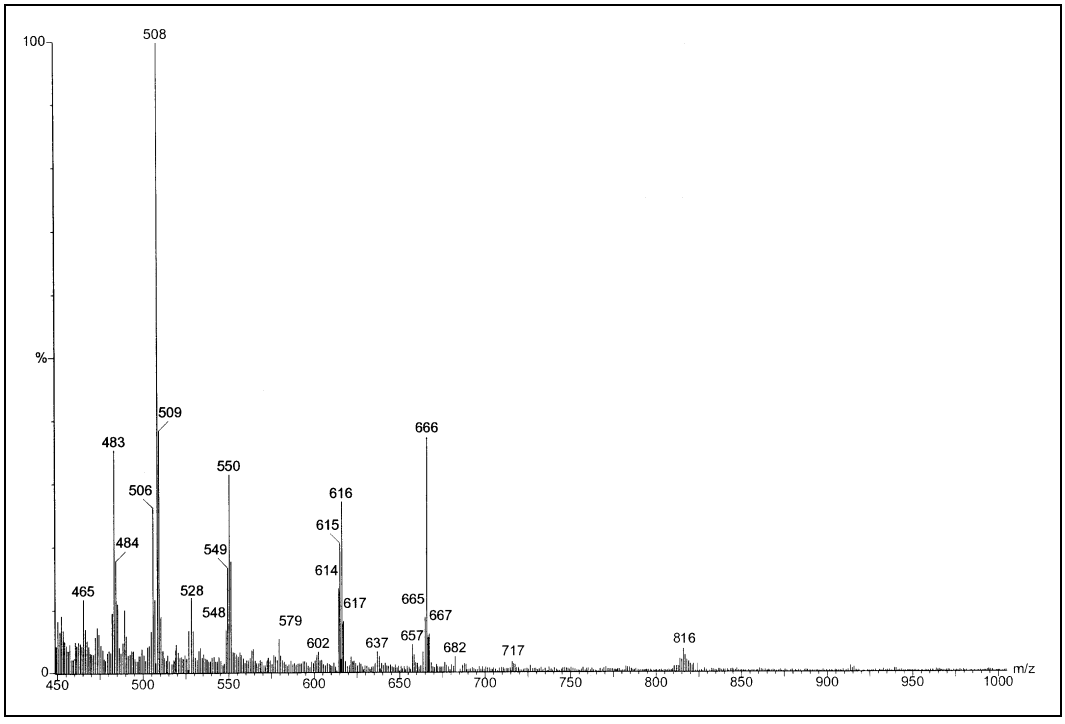


Figure S30: ESI-MS spectra of Zn^{II} complex of $\mathbf{L_9}$

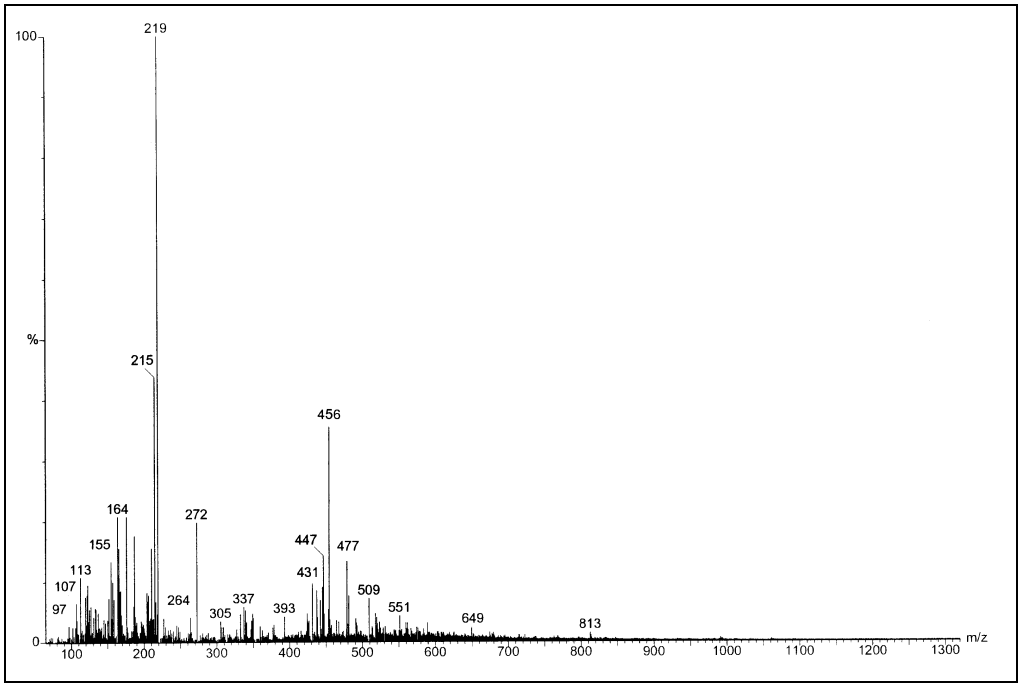


Figure S31: ESI-MS spectra of Zn^{II} complex of $\mathbf{L_{10}}$

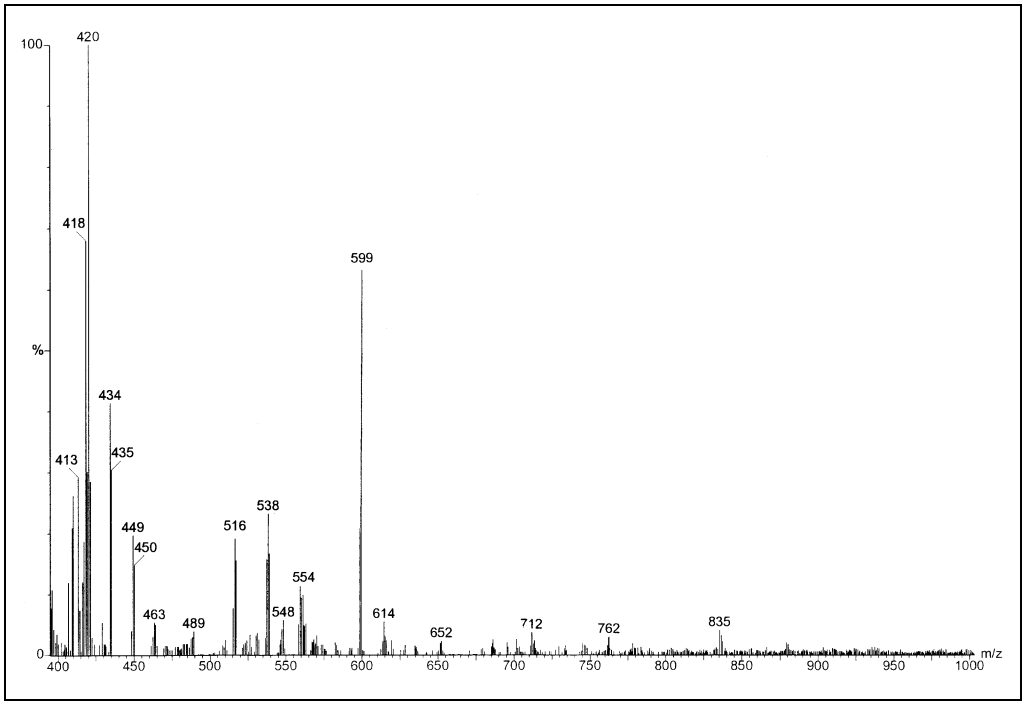


Figure S32: ESI-MS spectra of Zn^{II} complex of $\mathbf{L_{11}}$

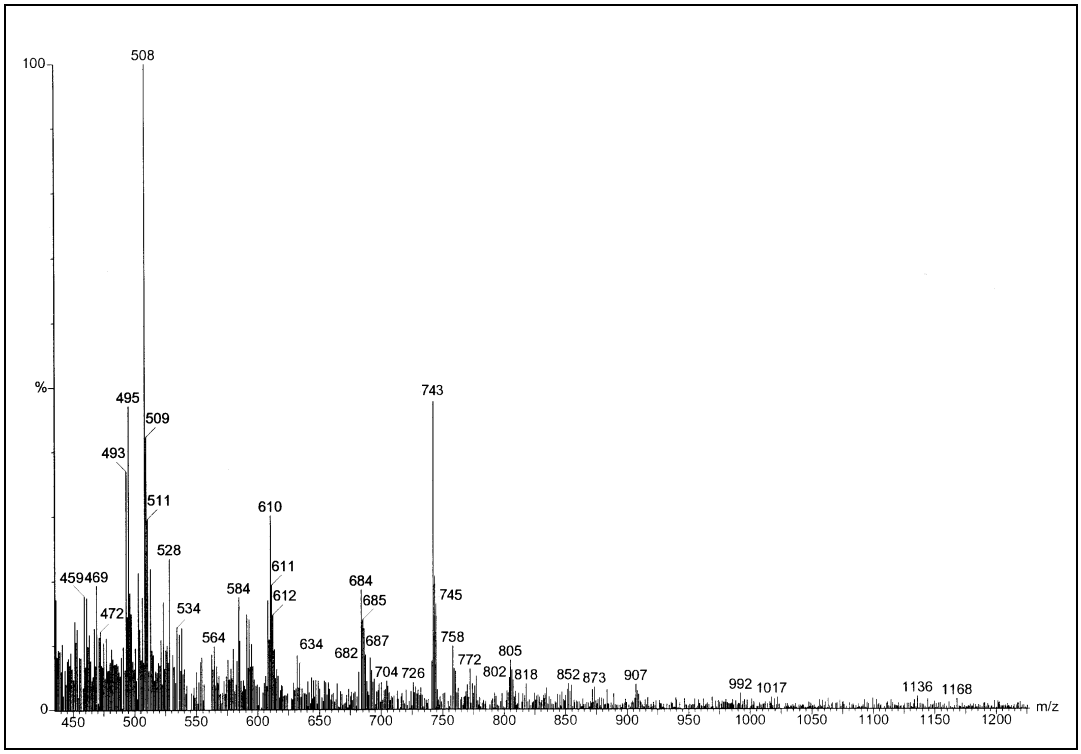


Figure S33: ESI-MS spectra of Zn^{II} complex of $\mathbf{L_{12}}$

Section 2: UV-vis spectra.

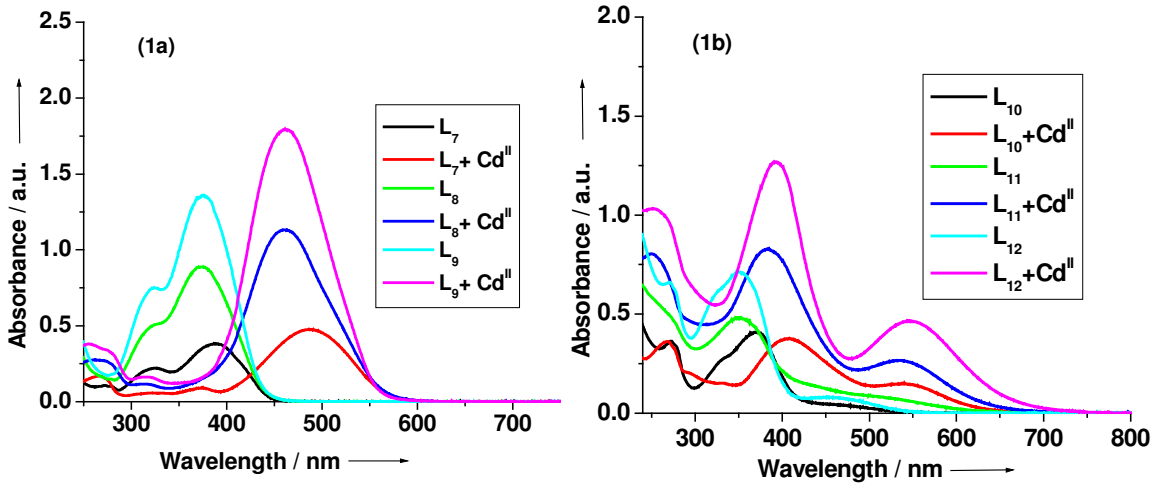


Figure S34. Absorption spectra of all the chromophores with Cd^{II} perchlorate in 10^{-5}(M) CH_3CN. (1a) with the chromophores $\mathbf{L_7}$ to $\mathbf{L_9}$ and (1b) with the chromophores $\mathbf{L_{10}}$ to $\mathbf{L_{12}}$.

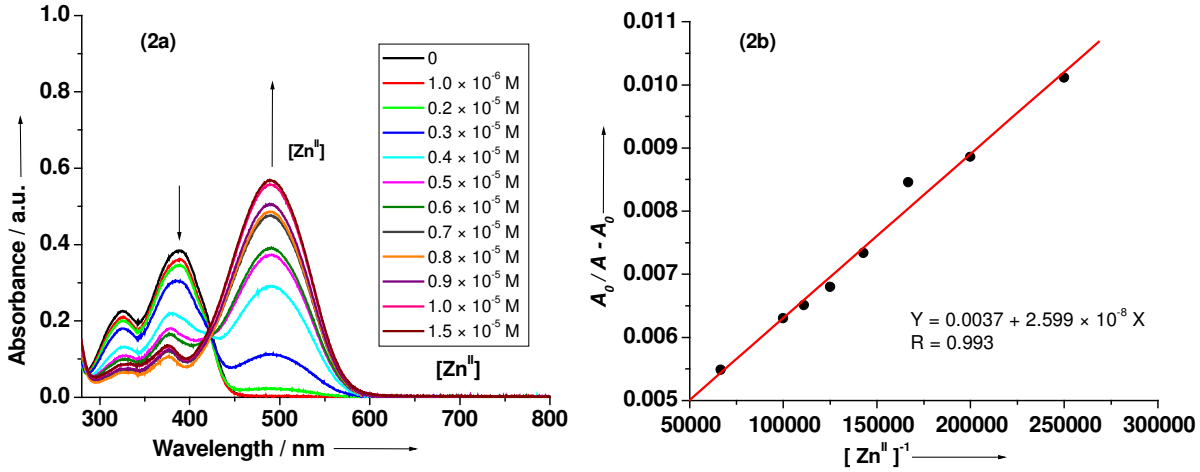


Figure S35. (2a) Absorption spectra of the chromophore $\mathbf{L_7}$ as a function of [Zn^{II}]. The arrows indicate the trend for increasing [Zn^{II}]. The [$\mathbf{L_7}$] is 1×10^{-5} (M). (2b) Plot of $A_0/A-A_0$ against [Zn^{II}]$^{-1}$ for binding constant determination. The absorption data yield log K_s = 5.153.

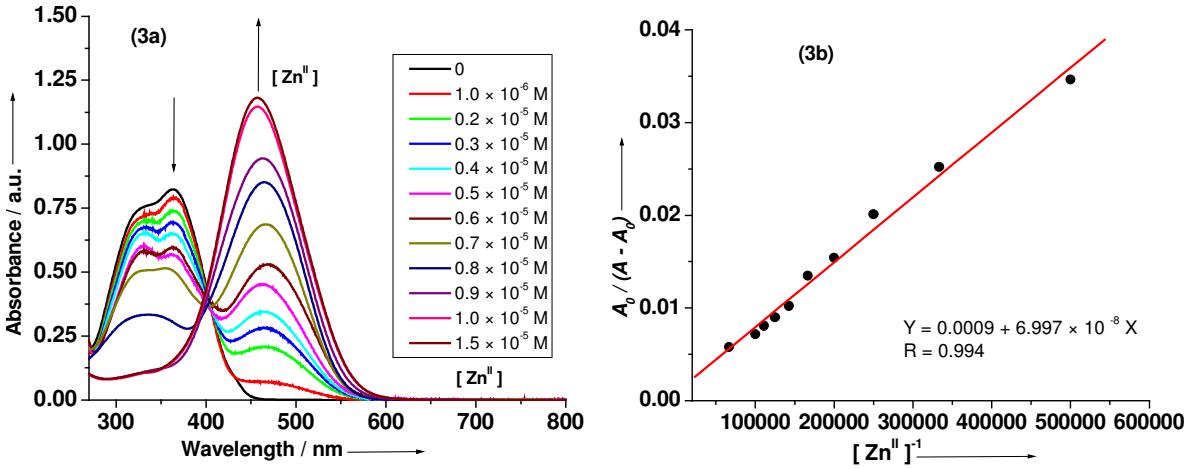


Figure S36. (3a) Absorption spectra of the chromophore $\mathbf{L_8}$ as a function of [Zn^{II}]. The arrows indicate the trend for increasing [Zn^{II}]. The [$\mathbf{L_8}$] is 1×10^{-5} (M). (3b) Plot of $A_0/A-A_0$ against [Zn^{II}]$^{-1}$ for binding constant determination. The absorption data yield log K_s = 4.13.

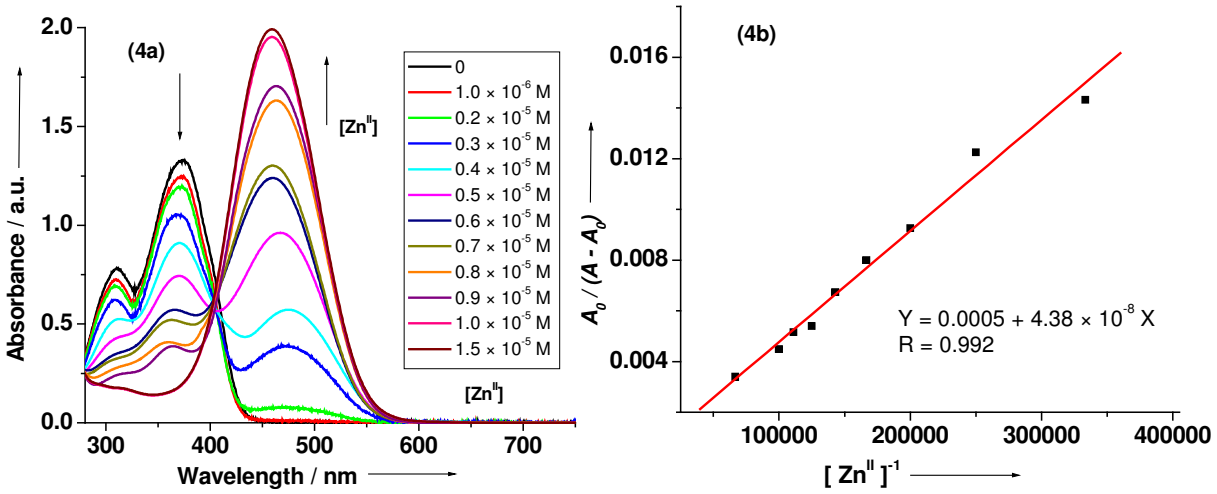


Figure S37. (4a) Absorption spectra of the chromophore $\mathbf{L_9}$ as a function of [Zn^{II}]. The arrows indicate the trend for increasing [Zn^{II}]. The [$\mathbf{L_9}$] is 1×10^{-5} (M). (4b) Plot of $A_0/A-A_0$ against [Zn^{II}]$^{-1}$ for binding constant determination. The absorption data yield log $K_s = 4.06$.

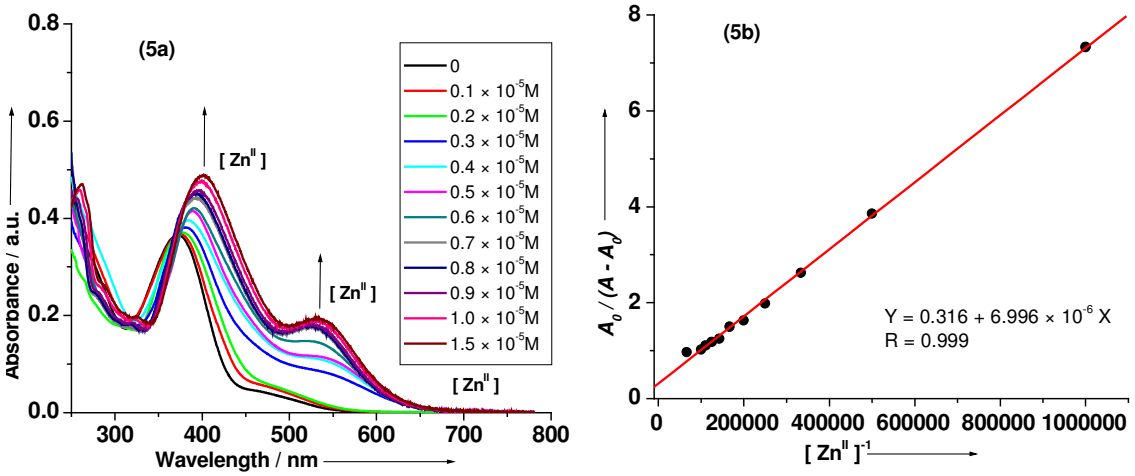


Figure S38. (5a) Absorption spectra of the chromophore $\mathbf{L_{10}}$ as a function of [Zn^{II}]. The arrows indicate the trend for increasing [Zn^{II}]. The [$\mathbf{L_{10}}$] is 1×10^{-5} (M). (5b) Plot of $A_0/A-A_0$ against [Zn^{II}]$^{-1}$ for binding constant determination. The absorption data yield log $K_s = 4.65$.

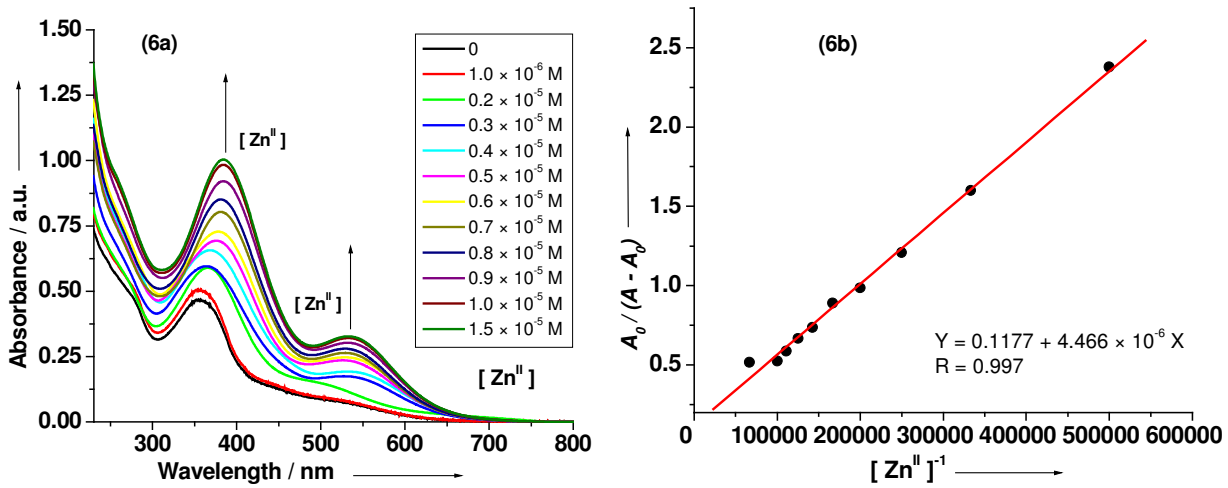


Figure S39. (6a) Absorption spectra of the chromophore $\mathbf{L_{11}}$ as a function of [Zn^{II}]. The arrows indicate the trend for increasing [Zn^{II}]. The [$\mathbf{L_{11}}$] is 1×10^{-5} (M). (6b) Plot of $A_0/A-A_0$ against [Zn^{II}]$^{-1}$ for binding constant determination. The absorption data yield log $K_s = 4.42$.

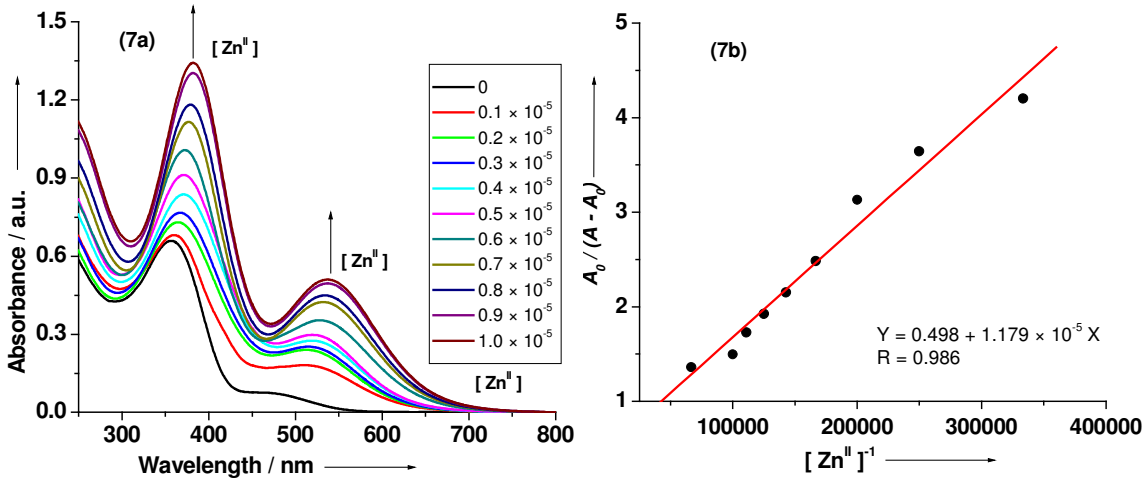


Figure S40. (7a) Absorption spectra of the chromophore $\mathbf{L_{12}}$ as a function of [Zn^{II}]. The arrows indicate the trend for increasing [Zn^{II}]. The [$\mathbf{L_{12}}$] is 1×10^{-5} (M). (7b) Plot of $A_0/A-A_0$ against [Zn^{II}]$^{-1}$ for binding constant determination. The absorption data yield log $K_s = 4.62$.

Section 3: Two-Photon Absorption Spectra.

Measurement of two-photon absorption cross-section ($\sigma^{(2)}$):

Two-photon absorption cross-section values were measured by the open aperture Z-Scan technique. All the experiments were carried out using 10^{-5} M solutions in dry acetonitrile after purging with argon for 10 min.

Two-photon absorption coefficient were measured by using an open aperture Z-scan method with ~130 fs pulses at 5 kHz repetition rate generated from a Ti:sapphire regenerative amplifier system (Spectra-Physics, Hurricane). The laser beam was divided into two parts. One was monitored by a Ge/PN photodiode as intensity reference and the other was used for transmittance measurement. After passing through an f = 10 cm lens, the laser beam was focused and passed through a quartz cell. The position of the sample cell could be varied along the laser-beam direction (z-axis), so the local power density within the sample cell could be changed under a constant laser power level. The thickness of the cell is 1 mm. The transmitted laser beam from the sample cell was then detected by the same photodiode as used for reference monitoring. The on-axis peak intensity of the incident pulses at the focal point, I_0, ranged from 40 to 80 GW/cm. Assuming a Gaussian beam profile, the nonlinear absorption coefficient β can be obtained by curve fitting to the observed open-aperture traces with the following equation:

$$T(z) = 1 - \frac{\beta I_0 (1 - e^{-\alpha_0 l})}{2\alpha_0 (1 + (z / z_0)^2)} \qquad (1)$$

where α_0 is the linear absorption coefficient, l the sample length, and z_0 the diffraction length of the incident beam. After obtaining the nonlinear absorption coefficient β, the TPA cross section

$\sigma^{(2)}$ of one solute molecule (in units of 1 GM = 10^{-50}cm^4·s/photon·molecule) can be determined by using the following relationship:

$$\beta = \frac{\sigma^{(2)} N_A d \times 10^{-3}}{h\nu} \qquad (2)$$

where N_A is the Avogadro constant, d is the concentration of the TPA compound in solution , h is the Planck constant, and ν is the frequency of the incident laser beam. So as to satisfy the condition of $a_0 l \ll 1$, which allows the pure TPA $\sigma^{(2)}$ values to be determined using a simulation procedure, the TPA cross-section value of AF-50 was measured as a reference compound; this control was found to exhibit a TPA value of 50 GM at 800 nm.

According to the basic consideration of the TPA process[1], the beam-intensity change along the propagation direction (z axis) can be described as

$$dI/dz + \alpha I + \beta I^2 = 0 \qquad (3)$$

where α is the linear absorption coefficient, β is the nonlinear absorption coefficient.

The solution of equation (3) is:

$$I(z) = \frac{I(0)\exp(-\alpha z)}{1 + (\beta/\alpha) I(0) - (\beta/\alpha) I(0)\exp(-\alpha z)} \qquad (4)$$

Where $I(0)$ is the initial intensity, z is the sample length.

Only in the case of small linear absorption, i.e., αz << 1, equation (4) becomes following equation from which our fitting equation is derived.

$$I(z) = \frac{I(0)\exp(-\alpha z)}{1 + \beta z I(0)} \qquad (5)$$

"Along the TPA equation, if the condition of $\alpha_0 l$ << 1 is satisfied, this means that linear absorption effect can't affect the two photon absorption property. We do TPA measurement where the linear absorption band is not existed and the one photon absorption does not affect the TPA resonance."

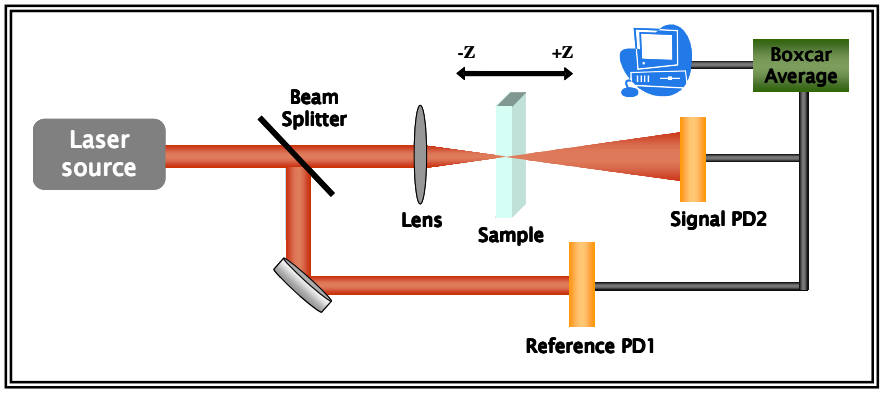


Figure S41. Schematic diagram of open aperture Z-scan experimental set-up.

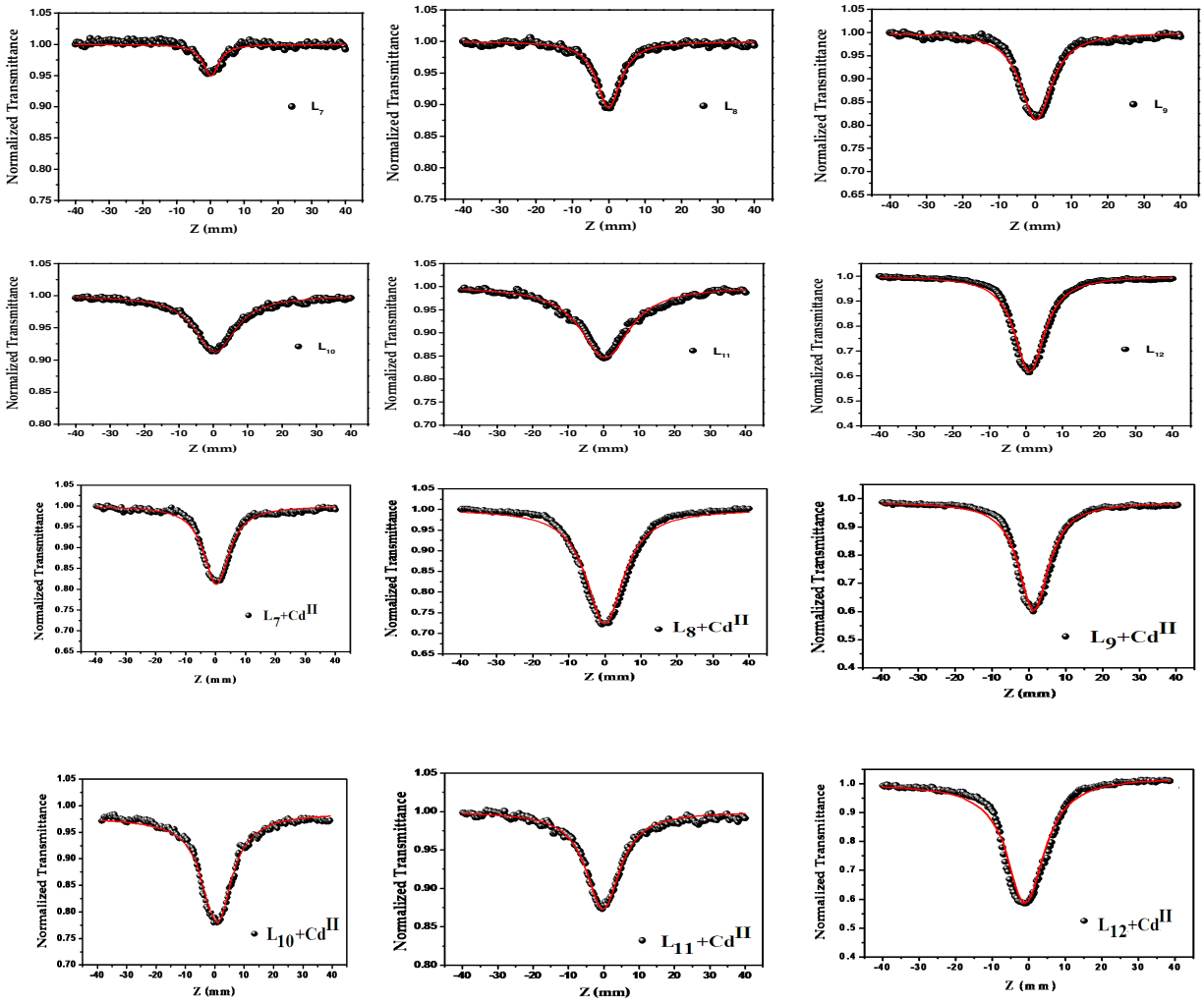


Figure S42. Theoretically fitted Open aperture Z-scan traces for all the ligands $\mathbf{L_7}$ to $\mathbf{L_{12}}$ and their corresponding Cd^{II} complexes.

$[Zn(\mathbf{L_7})](ClO_4)_2$: ($\sigma^{(2)}$= 1220 GM); $[Zn(\mathbf{L_8})](ClO_4)_2$: ($\sigma^{(2)}$= 2860 GM);

$[Zn(\mathbf{L_9})](ClO_4)_2$: ($\sigma^{(2)}$= 4640 GM); $[Zn(\mathbf{L_{10}})](ClO_4)_2$: ($\sigma^{(2)}$= 2700 GM);

$[Zn(\mathbf{L_{11}})](ClO_4)_2$: ($\sigma^{(2)}$= 7490GM); $[Zn(\mathbf{L_{12}})](ClO_4)_2$: ($\sigma^{(2)}$= 11200GM).

$[Cd(\mathbf{L_7})](ClO_4)_2$: ($\sigma^{(2)}$= 1300 GM); $[Cd(\mathbf{L_8})](ClO_4)_2$: ($\sigma^{(2)}$= 2750 GM);

$[Cd(\mathbf{L_9})](ClO_4)_2$: ($\sigma^{(2)}$=3990 GM); $[Cd(\mathbf{L_{10}})](ClO_4)_2$: ($\sigma^{(2)}$= 2560 GM);

$[Cd(\mathbf{L_{11}})](ClO_4)_2$: ($\sigma^{(2)}$= 6150GM); $[Cd(\mathbf{L_{12}})](ClO_4)_2$: ($\sigma^{(2)}$= 10660GM).

We did some additional experiments to demonstrate that the phenomenon is only the two-photon absorption process (not contaminated with other nonlinear effects).

Generally the transmittance changes in the Z-scan curves are associated with the combination of changes in the nonlinear refractive index and nonlinear absorption[2] (multiphoton absorption). However, in the open-aperture Z-scan method (the method used in the present investigation), the Z-scan transmittance changes are insensitive to beam distortion and is only a function of nonlinear absorption.[2] Since, the two-photon absorption is proportional to the square of the excitation intensity (quadratic relationship), we have carried out the irradiance-dependent transmittance changes for $\mathbf{L_9}$ in presence as well as the absence of Zn^{II} metal ion as an representative example. A linear relationship (Figure S43) of the transmittance change amplitude, ΔT, on the laser irradiance a typical of two-photon absorption process[2, 3] is observed.

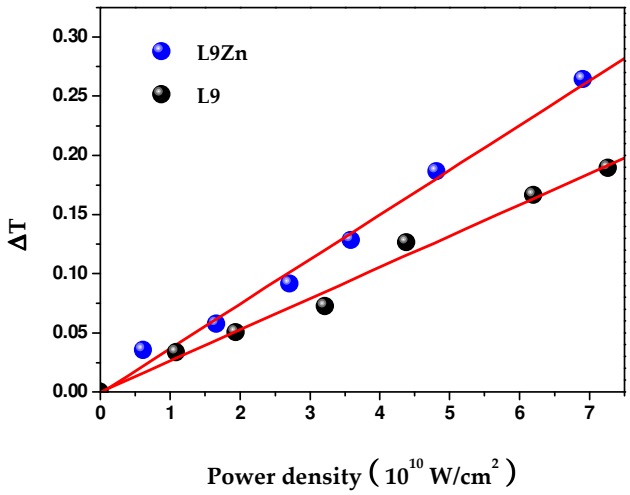


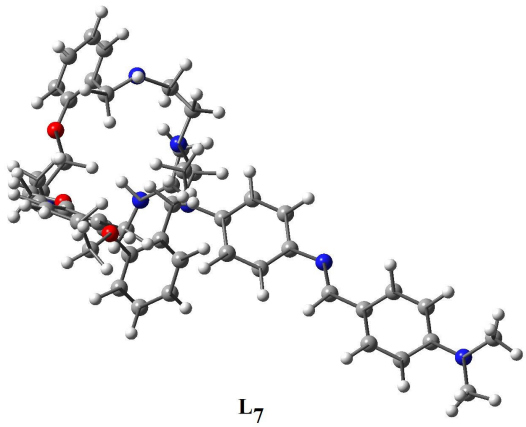
Figure S43. Plot of the transmittance change amplitude, ΔT, against power density for the chromophore **L$_9$** and its Zn^{II} complex.

Furthermore, the transmittance changes of **L$_9$** in presence of Zn^{II} metal ion also show linear relationship with laser irradiance again ascertaining that the transmittance changes are solely originated from the enhanced two-photon absorbing efficiency of the molecule. If the transmittance was accompanied by any other nonlinear effects, the change in transmittance with the laser irradiance might have deviated from linearity.[2] Hence, this experiment unambiguously confirms that the observed Z-scan transmittance changes are due to two-photon absorption processes.

Section 4: Results of the Theoretical Studies of Ligands and Their Corresponding Zn^{II} - complexes.

We employed a blend of quantum- chemical approaches to model both linear and non-linear spectra of the chromophores of interest. Geometry optimization has been carried out for all the ligands and their Zn^{II} complexes. Time dependent density functional theory is applied for obtaining the excitation energies and transition dipole moments. All calculations are performed by the GAUSSIAN 03 program[4] using the B3LYP functional with a 6–31G* basis set.

Optimized geometries, X, Y, Z Cartesian coordinates in Å unit for all the chromophores L_7 to L_9 and their corresponding Zn^{II} complexes in B3LYP/6–31G* level.



L_7

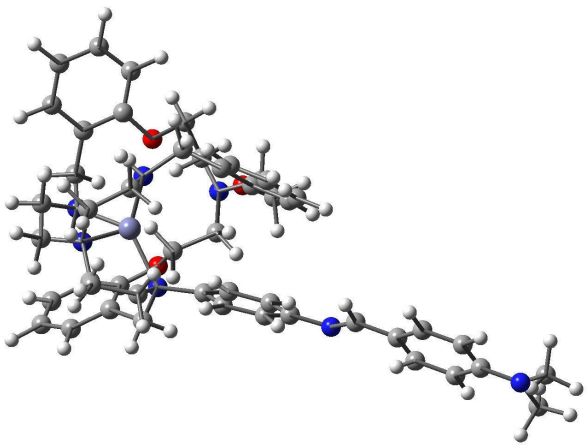
Table 1. Atomic numbers and the optimized X, Y, Z Cartesian parameters in Å unit for the ligand L_7

Atomic No	X	Y	Z
8	-5.472816	-2.108879	0.278857
8	-1.676505	-1.191286	2.603707
8	-4.714285	2.835495	0.926985
7	-2.184240	2.731443	-0.620665
7	-1.675487	0.598179	-2.607036
7	-4.652472	0.077725	2.351256

7	-4.137444	-1.073606	-3.645101
7	0.285761	-1.227633	0.040220
7	5.819814	-0.333744	-0.840325
7	12.202510	0.819936	-0.554959
6	-5.875110	-4.372748	-0.444893
6	-5.481528	-3.061697	-0.726179
6	-5.161345	-2.665993	-2.035275
6	-5.262821	-3.621988	-3.052181
6	-5.646367	-4.935723	-2.779139
6	-5.951523	-5.313784	-1.471124
6	-4.481005	-2.279560	1.302797
6	-4.806462	-1.373253	2.494527
6	-5.605144	0.651652	1.395570
6	-5.834966	2.157909	1.502189
6	-4.756502	4.170923	0.624637
6	-5.909149	4.957265	0.655528
6	-5.834019	6.301090	0.271734
6	-4.622764	6.856064	-0.129709
6	-3.470505	6.061365	-0.130294
6	-3.509708	4.720308	0.248231
6	-2.267024	3.848457	0.329742
6	-1.555280	3.061557	-1.891624
6	-1.779992	2.016028	-2.991462
6	-1.748852	-0.252238	-3.809240
6	-2.719106	-1.442250	-3.737986
6	-4.749997	-1.229389	-2.326915
6	-0.507846	0.300386	-1.763318
6	-0.589401	-1.098147	-1.131642
6	1.686761	-1.002245	-0.200971
6	2.379432	-1.601171	-1.266679
6	3.733693	-1.354851	-1.465513
6	4.455503	-0.537067	-0.578596
6	3.759831	0.070308	0.482665
6	2.397220	-0.158371	0.661244
6	12.762617	0.964993	-1.887567
6	13.069190	0.923310	0.605598
6	6.650005	-0.207228	0.132068
6	0.027886	-2.471430	0.802292
6	0.362247	-2.345171	2.273412
6	-0.502699	-1.649479	3.144218
6	-0.171061	-1.480604	4.491794
6	1.018166	-2.020466	4.989121
6	1.871615	-2.732357	4.150254
6	1.534697	-2.886592	2.802551
6	8.069863	0.061265	-0.062195
6	8.633702	0.220804	-1.341690

6	9.984615	0.468450	-1.508866
6	10.854275	0.573363	-0.391267
6	10.285266	0.415167	0.895515
6	8.928276	0.164956	1.043606
6	-2.241986	0.017991	3.124522
6	-3.275858	0.551902	2.138416
1	-2.472614	-2.094992	-2.895407
1	-1.036651	-2.695436	0.693434
1	0.583181	-3.325391	0.377728
1	-2.698821	-0.147778	4.109966
1	-6.571766	0.167536	1.573388
1	-1.900400	4.023880	-2.316716
1	-1.614545	-1.235978	-0.773029
1	-2.554418	-2.041195	-4.647813
1	-3.096502	2.305719	-0.751677
1	-0.841865	-0.945856	5.156043
1	1.265783	-1.886484	6.039052
1	2.794196	-3.157884	4.534579
1	2.2 04175	-3.425604	2.136514
1	-1.436154	0.753349	3.241280
1	-2.898305	0.361347	1.119289
1	-3.298649	1.636342	2.250437
1	-5.340871	0.434575	0.347488
1	-5.969877	2.475876	2.544773
1	-6.744631	2.400320	0.937500
1	-6.858321	4.541196	0.974497
1	-6.734731	6.908967	0.293168
1	-2.514851	6.496968	-0.414258
1	-4.566951	7.899180	-0.427402
1	-2.200755	3.439489	1.346018
1	-1.377448	4.473071	0.189582
1	-0.477599	3.179579	-1.710862
1	-1.076774	2.274309	-3.808589
1	-2.789357	2.153008	-3.404166
1	-0.504479	1.014986	-0.938717
1	0.438501	0.408731	-2.325669
1	-0.406888	-1.884327	-1.888397
1	-5.843734	-1.569014	2.794995
1	-4.169968	-1.702858	3.322294
1	-4.475922	-3.322282	1.649541
1	-3.486078	-2.059507	0.897682
1	-6.138416	-4.639995	0.574859
1	-6.259761	-6.332113	-1.248861
1	-5.030292	-3.309153	-4.065051
1	-5.711556	-5.659942	-3.586924
1	-4.103607	-0.863298	-1.514318

1	-5.648199	-0.596782	-2.303236
1	-0.745444	-0.625468	-4.082801
1	-2.067362	0.368597	-4.658667
1	1.850886	-2.255454	-1.955220
1	4.265870	-1.804497	-2.298765
1	4.281476	0.756999	1.143660
1	1.857117	0.326884	1.468044
1	6.328928	-0.312657	1.180561
1	7.981539	0.142492	-2.206037
1	10.373936	0.583282	-2.513581
1	10.904749	0.485702	1.781470
1	8.521355	0.045894	2.046022
1	13.835963	1.144342	-1.807508
1	12.615065	0.060317	-2.494031
1	12.317840	1.811735	-2.429133
1	14.089903	1.122768	0.275404
1	12.763512	1.742283	1.272064
1	13.079055	-0.005378	1.194047
1	-4.269748	-0.119408	-3.966105



L_7 +Zn(II)

Table 2. Atomic numbers and the optimized X, Y, Z Cartesian parameters in Å unit for the Zn^{II} complex of L_7

Atomic No	X	Y	Z
30	-2.414159	0.625715	-0.770301
8	-1.752176	1.599664	2.134627
8	-3.532336	-2.103140	1.770135
8	0.111248	-2.070488	0.642064

7	-1.132303	-1.349398	3.145430
7	-0.719858	1.950214	-0.986251
7	-3.246381	1.506866	-2.551333
7	-4.466960	0.814354	-0.052355
7	11.264040	-0.068847	0.536368
7	4.806172	0.857785	0.248777
7	-2.458929	-1.193572	-1.766015
6	-0.802576	-0.044449	3.756185
6	-1.833086	1.072420	3.507081
6	-2.581418	2.666277	1.809586
6	-3.716006	3.025058	2.573591
6	-4.544082	4.089525	2.168443
6	-4.255090	4.812835	1.001151
6	-3.116612	4.466672	0.254096
6	-2.263647	3.398931	0.620127
6	-0.940208	3.230682	-0.105042
6	-0.880566	2.304286	-2.458150
6	-2.311340	2.626158	-2.893531
6	-4.634562	1.996928	-2.251614
6	-5.321278	1.045108	-1.270320
6	-5.218167	-0.088645	0.939051
6	-5.445014	-1.522480	0.501841
6	-6.565343	-1.911015	-0.269135
6	-6.820183	-3.260402	-0.564350
6	-5.959292	-4.252035	-0.062189
6	-4.851232	-3.903169	0.728941
6	-4.595062	-2.545361	1.009664
6	-3.019527	-2.955736	2.830497
6	-2.265111	-2.040081	3.804479
6	0.035858	-2.260231	3.054502
6	0.938701	-2.047706	1.832669
6	0.700177	-2.302555	-0.584926
6	2.091527	-2.389103	-0.796161
6	2.589122	-2.675888	-2.078349
6	1.716902	-2.887654	-3.158603
6	0.333280	-2.799857	-2.943043
6	-0.201762	-2.487633	-1.673417
6	-1.693841	-2.497204	-1.434570
6	-2.336795	-0.799116	-3.215279
6	-3.267722	0.384283	-3.567307
6	5.690115	0.311782	-0.555533
6	0.718215	1.508684	-0.766079
6	3.486802	1.030619	-0.150310
6	1.702720	1.527341	-1.781303
6	2.482521	1.038580	0.859682
6	9.345484	-0.524174	-0.919462

6	9.915202	0.023019	0.277806
6	9.021963	0.671410	1.199325
6	1.135280	1.242683	0.557371
6	11.831031	0.500839	1.771307
6	12.163630	-0.733118	-0.422750
6	7.981766	-0.423960	-1.166313
6	7.663862	0.763880	0.935719
6	7.098319	0.220267	-0.255089
6	3.050862	1.280830	-1.480446
1	0.176721	0.283409	3.374400
1	-0.692264	-0.113838	4.864310
1	-2.854756	0.702939	3.687591
1	-1.637671	1.908350	4.200182
1	-3.953949	2.499054	3.497758
1	-5.406846	4.356051	2.784561
1	-4.879738	5.655834	0.697734
1	-2.845334	5.077110	-0.613560
1	-0.765513	4.100503	-0.758013
1	-0.132142	3.218058	0.632900
1	-0.511521	1.444993	-3.032669
1	-0.231226	3.162143	-2.699904
1	-2.313933	2.834112	-3.979525
1	-2.671482	3.532750	-2.389631
1	-5.234857	2.100728	-3.173542
1	-4.552905	2.994583	-1.795864
1	-6.301972	1.461908	-0.978358
1	-5.514773	0.063801	-1.728901
1	-6.189606	0.400029	1.133199
1	-4.627511	-0.072689	1.862217
1	-7.274251	-1.147701	-0.605232
1	-7.696615	-3.536337	-1.154905
1	-6.155794	-5.306712	-0.272029
1	-4.199965	-4.682170	1.129939
1	-2.362688	-3.730973	2.400272
1	-3.857552	-3.454880	3.347727
1	-2.979906	-1.293501	4.182792
1	-1.945230	-2.642216	4.683834
1	-0.347567	-3.290153	3.003613
1	0.676758	-2.213539	3.963605
1	1.489593	-1.096415	1.871459
1	1.674164	-2.871101	1.805640
1	-2.165873	-3.283774	-2.048899
1	-1.914925	-2.688461	-0.377713
1	2.790302	-2.230861	0.024719
1	-0.352426	-3.012801	-3.769837
1	2.106097	-3.138464	-4.147911

1	3.670355	-2.747602	-2.223839
1	-4.303147	0.015938	-3.630922
1	-3.006667	0.770504	-4.568357
1	-1.279225	-0.564706	-3.397578
1	-2.595841	-1.649927	-3.870786
1	-4.411186	1.718833	0.442958
1	-3.445559	-1.459771	-1.604062
1	1.472867	1.760004	-2.819757
1	0.396958	1.237526	1.357666
1	3.784403	1.342210	-2.287680
1	2.802698	0.886149	1.894018
1	5.378541	-0.140056	-1.520399
1	7.001398	1.261765	1.647563
1	7.578176	-0.849579	-2.091418
1	9.409464	1.102676	2.122338
1	9.979744	-1.024387	-1.650879
1	11.664823	1.591299	1.825985
1	11.391165	0.032488	2.669528
1	12.912471	0.318292	1.785362
1	13.189812	-0.694866	-0.037412
1	11.888111	-1.793166	-0.565441
1	12.145316	-0.230099	-1.405824

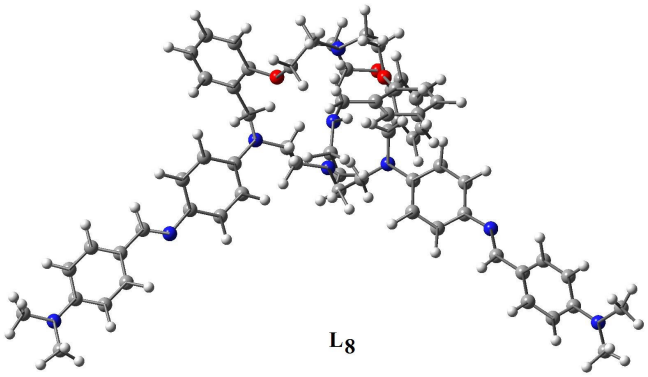


Table 3. Atomic numbers and the optimized X, Y, Z Cartesian parameters in Å unit for the ligand L_8

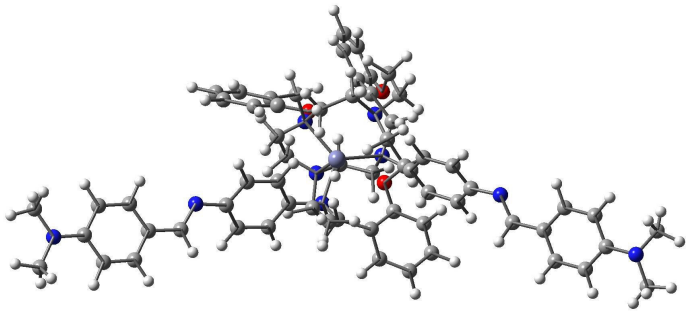
Atomic No	X	Y	Z
8	-2.501064	-4.093513	-0.261808
8	1.717588	-4.377449	2.321663
8	2.531781	-4.203061	-1.515638
7	0.230288	-5.399075	-0.032806

7	0.389905	-2.238917	-2.569315
7	-0.092100	-0.116106	-0.562320
7	2.367950	-0.283924	1.234396
7	7.200151	2.492129	0.233968
7	12.216430	6.554192	-0.521868
7	-3.539991	-1.264248	0.521766
7	-7.298472	2.948226	0.009420
7	-12.428659	6.908939	-0.434034
6	2.467024	-3.945418	4.552578
6	2.247382	-3.494828	3.250022
6	2.590164	-2.189893	2.859121
6	3.153543	-1.350403	3.827778
6	3.374511	-1.790893	5.134158
6	3.033960	-3.093047	5.499616
6	0.285574	-4.413980	2.275681
6	-0.180833	-5.542749	1.369001
6	1.529370	-6.033470	-0.276198
6	2.244345	-5.606120	-1.551932
6	3.188510	-3.725005	-2.641710
6	4.581688	-3.738379	-2.682466
6	5.248726	-3.208616	-3.789280
6	4.518204	-2.672833	-4.849479
6	3.121877	-2.663244	-4.796975
6	2.431729	-3.185451	-3.697683
6	0.916735	-3.149238	-3.591484
6	0.329434	-0.836172	-2.977058
6	0.586573	0.152686	-1.838603
6	0.286181	0.921363	0.415874
6	1.134210	0.409140	1.595312
6	3.550774	0.416001	0.999698
6	4.798595	-0.241395	0.879110
6	5.962661	0.465673	0.614116
6	5.972784	1.865179	0.495739
6	4.736279	2.523130	0.609829
6	3.559160	1.823108	0.850760
6	2.353366	-1.729202	1.419892
6	7.418448	3.698925	0.617834
6	8.654688	4.415225	0.319468
6	9.691964	3.837547	-0.435204
6	10.862063	4.527374	-0.702491
6	11.056924	5.851955	-0.232739
6	10.017338	6.428147	0.534377
6	8.850609	5.721102	0.794241
6	13.334765	5.869545	-1.148369
6	-1.544714	-0.313340	-0.678157
6	-2.112754	-0.947136	0.603200

6	-4.466573	-0.203497	0.394661
6	-4.140986	1.141675	0.657513
6	-5.085494	2.152105	0.508320
6	-6.408892	1.870556	0.136060
6	-6.734539	0.528347	-0.137720
6	-5.785391	-0.479522	-0.020658
6	-8.554224	2.787720	0.229595
6	-3.972604	-2.382689	1.392779
6	-4.583408	-3.600257	0.716915
6	-3.810402	-4.452576	-0.100414
6	-4.380864	-5.601166	-0.662395
6	-5.722934	-5.906134	-0.422395
6	-6.498479	-5.081825	0.387551
6	-5.916249	-3.944195	0.952559
6	-1.733982	-4.616347	-1.359455
6	-0.825425	-5.786336	-0.973565
6	12.458333	7.833867	0.121693
6	-12.050157	8.168680	-1.051795
6	-13.839346	6.600564	-0.277062
6	-9.534544	3.853406	0.050737
6	-9.173195	5.134575	-0.404881
6	-10.115711	6.134364	-0.571223
6	-11.486749	5.905520	-0.284580
6	-11.850364	4.613571	0.163720
6	-10.891036	3.623266	0.327337
1	0.531946	-0.288243	2.185290
1	-3.095285	-2.705769	1.964273
1	-4.698469	-2.006188	2.124673
1	1.080007	-0.595237	-3.749215
1	-1.584589	-1.892369	0.738345
1	1.357189	1.257197	2.258967
1	0.907617	-2.352570	-1.701556
1	-3.783817	-6.269734	-1.272456
1	-6.151332	-6.800835	-0.866776
1	-7.540037	-5.319082	0.583655
1	-6.512924	-3.295310	1.590108
1	5.128986	-4.150249	-1.839270
1	6.334898	-3.211113	-3.817434
1	2.553894	-2.246248	-5.625903
1	5.031391	-2.257256	-5.712248
1	0.538792	-4.156453	-3.378377
1	0.486392	-2.860135	-4.557212
1	-0.651889	-0.643977	-3.434770
1	4.866630	-1.315241	1.004623
1	6.907289	-0.062279	0.519289
1	4.681346	3.599350	0.469046

1	2.634267	2.384410	0.903891
1	6.681684	4.262428	1.212239
1	9.558040	2.825115	-0.803433
1	11.634578	4.035090	-1.281279
1	10.118842	7.431090	0.931311
1	8.070135	6.194301	1.387287
1	11.668073	8.553998	-0.123274
1	13.402377	8.244239	-0.241703
1	12.516710	7.754212	1.218895
1	13.050230	5.461034	-2.125548
1	13.724902	5.042271	-0.534779
1	14.143740	6.583845	-1.313040
1	0.334756	1.159738	-2.228241
1	1.660582	0.162420	-1.620201
1	-1.733282	-1.018625	-1.490258
1	-2.070225	0.625369	-0.924094
1	-1.885913	-0.320186	1.484588
1	2.197095	-4.967838	4.802047
1	3.209062	-3.445863	6.512445
1	3.426822	-0.337484	3.551322
1	3.817243	-1.116200	5.861799
1	1.385535	-2.090666	1.065269
1	3.078440	-2.198686	0.747798
1	-0.611631	1.393431	0.839395
1	0.826567	1.727657	-0.096761
1	-3.143160	1.408799	0.987097
1	-4.817518	3.185955	0.706500
1	-7.728590	0.278124	-0.498930
1	-6.051752	-1.495970	-0.288335
1	-8.962775	1.827241	0.581988
1	-8.128320	5.325803	-0.628869
1	-9.788586	7.103154	-0.929789
1	-12.885024	4.379833	0.383935
1	-11.203874	2.640434	0.675075
1	-12.916891	8.831903	-1.071049
1	-11.260822	8.670494	-0.478490
1	-11.691087	8.042273	-2.084955
1	-14.422801	7.513283	-0.411066
1	-14.193577	5.855516	-1.006623
1	-14.050776	6.215986	0.728536
1	-2.407958	-4.909061	-2.173539
1	-1.120962	-3.776137	-1.698731
1	-1.419712	-6.637123	-0.595004
1	-0.362897	-6.129843	-1.906264
1	-1.272980	-5.536646	1.414649
1	0.155248	-6.507984	1.789705

1	-0.102505	-3.457239	1.902252
1	-0.110857	-4.575847	3.289286
1	2.173334	-5.781096	0.567974
1	1.450885	-7.140263	-0.309985
1	1.657887	-5.839496	-2.451968
1	3.182599	-6.175545	-1.625560



L_8+Zn(II)

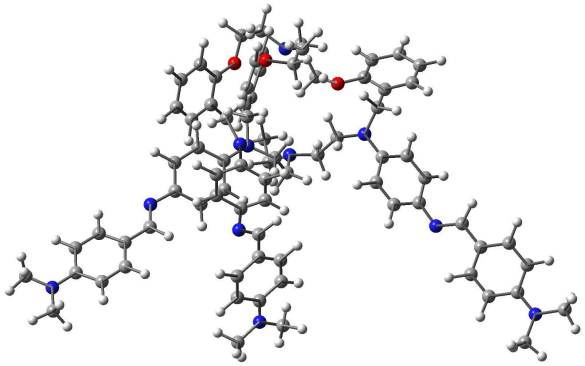
Table 4. Atomic numbers and the optimized X, Y, Z Cartesian parameters in Å unit for Zn^{II} complex of L_8

Atomic No	X	Y	Z
30	-0.190425	1.097280	-1.114065
8	1.521984	3.533748	0.899330
8	-1.825092	1.898416	2.557463
8	1.577555	-0.856151	1.707177
7	0.969880	1.653644	3.282271
7	1.839884	1.643242	-1.929567
7	-0.857384	1.129278	-3.128578
7	-1.603317	2.652123	-0.910204
7	-0.790014	-0.943565	-1.075202
7	6.778268	-0.528355	-0.084234
7	12.553941	-3.289032	0.943936
7	-12.526726	-3.582752	0.438455
7	-6.365788	-1.601018	-0.066179
6	2.035329	2.653041	3.123291
6	1.637792	3.874690	2.295759
6	1.084069	4.490735	0.022663
6	0.467386	5.685895	0.414107
6	-0.016771	6.576103	-0.547069
6	0.117531	6.297901	-1.906241

6	0.782648	5.133401	-2.291973
6	1.272123	4.208925	-1.354870
6	2.247623	3.139207	-1.781904
6	1.588103	1.362144	-3.381766
6	0.228763	1.831808	-3.857228
6	-2.145237	1.889706	-3.221805
6	-2.702466	2.265659	-1.843656
6	-2.117349	3.440124	0.295999
6	-3.310469	2.923049	1.056460
6	-4.614821	3.287183	0.698706
6	-5.713972	2.927990	1.477119
6	-5.509111	2.206363	2.652188
6	-4.219955	1.842523	3.047042
6	-3.124578	2.206244	2.256629
6	-1.462687	1.548802	3.897728
6	-0.088179	2.139162	4.182140
6	1.464020	0.366417	3.795249
6	2.325161	-0.473782	2.865349
6	2.086074	-1.852779	0.912652
6	3.371071	-2.387212	1.060928
6	3.807114	-3.404334	0.212298
6	2.971762	-3.908667	-0.783273
6	1.684828	-3.392822	-0.906299
6	1.220779	-2.357039	-0.081394
6	-0.235646	-1.988498	-0.076300
6	-0.339916	-1.258270	-2.464763
6	-0.955465	-0.314282	-3.511560
6	3.045727	0.877060	-1.485146
6	3.917049	0.230579	-2.371566
6	3.439366	1.014102	-0.146996
6	5.138729	-0.276142	-1.927406
6	4.673969	0.554211	0.279043
6	7.371998	-1.581878	-0.551810
6	8.688976	-2.003719	-0.151207
6	9.473100	-1.265869	0.763986
6	9.245027	-3.185669	-0.682641
6	10.735945	-1.681920	1.126437
6	13.112678	-4.513119	0.380436
6	-4.399739	-2.080585	-1.483054
6	-5.018054	-1.485774	-0.363769
6	-6.976808	-2.730199	-0.247448
6	-2.262892	-1.073477	-0.917843
6	-2.861796	-0.487214	0.202963
6	-3.044059	-1.894286	-1.742875
6	-4.213378	-0.674067	0.463681
6	-8.391317	-2.922894	-0.061889

6	-9.260692	-1.869528	0.298769
6	-8.956102	-4.201956	-0.245639
6	-10.613125	-2.078938	0.463696
6	-10.308885	-4.430680	-0.085406
6	-11.186402	-3.371462	0.276152
6	-13.090554	-4.914257	0.242928
6	-13.410360	-2.480512	0.802060
6	10.509366	-3.617928	-0.331646
6	11.300797	-2.876013	0.588504
6	13.353695	-2.504712	1.878759
6	5.553865	-0.124550	-0.591465
1	9.061251	-0.352750	1.182130
1	2.782291	1.531322	0.540995
1	6.871134	-2.232309	-1.286576
1	8.666971	-3.773858	-1.392770
1	3.702399	0.133437	-3.428203
1	11.301836	-1.083657	1.829723
1	10.893165	-4.529904	-0.771080
1	2.900284	2.182660	2.648962
1	2.389823	3.035286	4.099793
1	0.687710	4.284058	2.649530
1	2.404533	4.651480	2.404190
1	0.362143	5.939622	1.461437
1	-0.489211	7.498376	-0.222101
1	-0.238590	6.999816	-2.653169
1	0.985437	4.965993	-3.347743
1	2.682968	3.425613	-2.744532
1	3.057293	3.139909	-1.058167
1	1.671991	0.287032	-3.537678
1	2.366933	1.829600	-3.994433
1	0.142122	1.664837	-4.940032
1	0.116884	2.903096	-3.682473
1	-2.894950	1.312188	-3.769443
1	-1.963008	2.796909	-3.804952
1	-3.403275	3.098730	-1.971604
1	-3.249893	1.441126	-1.388761
1	-2.360949	4.435353	-0.091252
1	-1.267812	3.531348	0.967609
1	-4.770879	3.889358	-0.193300
1	-6.714634	3.222423	1.178721
1	-6.353515	1.921722	3.272823
1	-4.081357	1.271372	3.958076
1	-1.485937	0.457783	4.004189
1	-2.173075	1.977264	4.612598
1	-0.181949	3.222810	4.080974
1	0.161450	1.949325	5.242225

1	0.591844	-0.238334	4.060499
1	2.045106	0.503791	4.727993
1	3.237641	0.046973	2.559225
1	2.626647	-1.369398	3.423096
1	-0.824176	-2.889187	-0.278685
1	-0.521645	-1.614669	0.905083
1	4.044209	-2.014062	1.821793
1	1.003782	-3.833246	-1.631116
1	3.304031	-4.714699	-1.429478
1	4.807220	-3.806647	0.344213
1	-2.008510	-0.556251	-3.647369
1	-0.458118	-0.482685	-4.474515
1	0.750926	-1.206432	-2.455598
1	-0.590215	-2.290032	-2.735844
1	-1.042568	3.361448	-1.393651
1	5.803380	-0.740323	-2.649124
1	5.002457	0.707195	1.302795
1	13.544452	-1.493715	1.496891
1	12.862957	-2.419995	2.856683
1	14.315043	-2.996776	2.025739
1	14.109409	-4.673651	0.791199
1	12.498051	-5.387362	0.629961
1	13.200619	-4.451225	-0.711928
1	-2.263112	0.111011	0.885053
1	-2.623248	-2.411038	-2.598398
1	-4.675289	-0.202081	1.322383
1	-4.990728	-2.683462	-2.165449
1	-6.414121	-3.630668	-0.539795
1	-8.842432	-0.878847	0.447372
1	-8.311559	-5.033899	-0.522095
1	-11.242867	-1.242640	0.740776
1	-10.694225	-5.430611	-0.238882
1	-14.432054	-2.852511	0.878152
1	-13.134582	-2.045124	1.771073
1	-13.394253	-1.684573	0.046550
1	-12.927315	-5.274363	-0.780899
1	-12.655230	-5.641446	0.940044
1	-14.165234	-4.877253	0.420955



L_9

Table 5. Atomic numbers and the optimized X, Y, Z Cartesian parameters in Å unit for the ligand L_9

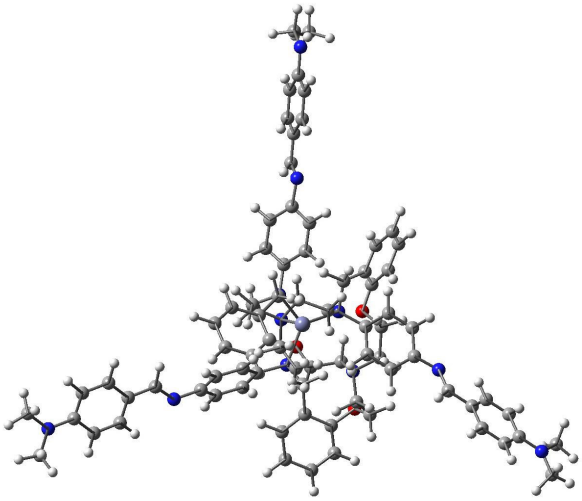
Atomic No	X	Y	Z
8	-2.128586	-4.031043	-2.605211
8	2.438786	-5.565908	-1.426073
8	2.333862	-2.807590	-4.996218
7	0.651797	-4.894311	-3.723049
7	0.169617	-1.371257	0.200558
7	-0.361332	5.750587	-3.469645
7	-3.489990	11.389931	-4.235110
7	-12.258317	1.659989	6.578618
7	1.477529	0.419863	-2.880684
7	-3.158657	-3.190770	0.230113
7	-7.038559	-0.549536	3.408386
7	11.870196	4.706831	5.511739
7	2.915142	-2.256950	1.260366
7	7.354289	0.880696	2.833301
6	3.469478	-7.038504	0.147115
6	3.095228	-5.742927	-0.215358
6	3.399094	-4.641196	0.602886
6	4.076654	-4.891653	1.802910
6	4.451493	-6.184024	2.174031
6	4.152250	-7.262729	1.342007
6	1.008301	-5.646706	-1.348486
6	0.409753	-5.937463	-2.717293
6	1.843709	-5.206896	-4.515292
6	2.287405	-4.130888	-5.512669
6	3.383181	-2.387908	-4.217825
6	4.502233	-3.175466	-3.919259
6	5.534410	-2.652823	-3.137901
6	5.455559	-1.353355	-2.639099
6	4.333078	-0.579244	-2.936343

6	3.292312	-1.068014	-3.729067
6	2.109964	-0.177425	-4.071711
6	0.709624	-0.561545	-2.114486
6	0.728877	-0.275136	-0.607547
6	0.600698	-1.250822	1.606714
6	1.669971	-2.279724	2.021083
6	3.998027	-1.476340	1.660667
6	5.297406	-1.677632	1.137954
6	6.362536	-0.879892	1.532566
6	6.216776	0.133649	2.494175
6	4.925277	0.344381	3.008258
6	3.845645	-0.431755	2.602423
6	3.015496	-3.225363	0.174334
6	7.461155	1.435364	3.987659
6	8.598614	2.268930	4.363704
6	9.654383	2.540141	3.474247
6	10.730511	3.326503	3.848006
6	10.805817	3.899627	5.143769
6	9.748085	3.619271	6.040303
6	8.676844	2.826675	5.649083
6	13.017727	4.834137	4.629684
6	-1.287037	-1.520070	0.058268
6	-1.739550	-2.930344	0.473025
6	-4.118441	-2.527906	1.022384
6	-3.780674	-1.777288	2.167444
6	-4.756772	-1.130343	2.917587
6	-6.118924	-1.229192	2.595666
6	-6.457991	-1.962554	1.443312
6	-5.484258	-2.586814	0.673510
6	0.960966	1.730398	-3.026799
6	-0.351616	2.086662	-2.669857
6	-0.809311	3.396854	-2.808724
6	0.019829	4.408146	-3.318168
6	1.344812	4.060774	-3.639351
6	1.801761	2.759097	-3.503924
6	-1.570504	6.051020	-3.783337
6	-2.046631	7.425701	-3.891336
6	-3.371246	7.688287	-4.273822
6	-3.857737	8.983585	-4.386577
6	-3.022753	10.094529	-4.118981
6	-1.684626	9.827633	-3.727937
6	-1.217163	8.529495	-3.619902
6	-4.878021	11.632008	-4.585265
6	-2.629804	12.509222	-3.893749
6	-0.544641	-4.527091	-4.479990
6	-8.233555	-0.998483	3.556747

6	-3.487586	-4.569475	-0.188962
6	-4.112980	-4.767781	-1.563631
6	-3.404178	-4.510140	-2.757211
6	-3.995810	-4.770638	-3.999511
6	-5.292911	-5.284860	-4.066925
6	-6.002519	-5.557023	-2.901946
6	-5.399908	-5.301330	-1.668175
6	-1.419819	-3.509779	-3.737751
6	11.997484	5.143080	6.891151
6	-9.253234	-0.303844	4.335025
6	-9.005103	0.930871	4.962773
6	-9.983153	1.576466	5.698946
6	-11.279232	1.016527	5.846376
6	-11.528395	-0.224749	5.213603
6	-10.534126	-0.858804	4.480998
6	-11.974177	2.932438	7.217950
6	-13.574014	1.062518	6.715636
1	1.242167	-3.283400	1.918413
1	-2.560792	-5.151830	-0.142006
1	-4.168682	-5.011602	0.549303
1	-2.127395	-3.034500	-4.426946
1	1.723277	-6.139497	-5.107769
1	-1.173238	-3.627039	-0.144723
1	1.890979	-2.145531	3.088370
1	-3.451436	-4.593384	-4.919416
1	-5.735707	-5.479472	-5.040164
1	-7.007471	-5.966179	-2.946796
1	-5.944689	-5.516678	-0.751378
1	-0.763818	-2.739149	-3.330266
1	2.643357	-5.394498	-3.795671
1	1.590909	-4.062646	-6.353473
1	3.258123	-4.424149	-5.934640
1	4.576562	-4.194366	-4.280021
1	6.397442	-3.275344	-2.916455
1	4.245977	0.427385	-2.536253
1	6.248596	-0.948200	-2.018310
1	2.445402	0.635996	-4.719839
1	-0.319224	-0.650003	-2.501841
1	5.482421	-2.472776	0.425891
1	7.352018	-1.051471	1.117915
1	4.746825	1.158859	3.705175
1	2.866769	-0.197921	3.004587
1	6.698820	1.300740	4.771376
1	9.611065	2.110950	2.478056
1	11.521943	3.500350	3.128574
1	9.761129	4.019516	7.046979

1	7.879114	2.630889	6.363340
1	11.125137	5.731590	7.201545
1	12.877301	5.782446	6.985019
1	12.106500	4.302061	7.594145
1	12.726095	5.251544	3.658076
1	13.522797	3.872434	4.448189
1	13.739601	5.518590	5.079259
1	0.229632	0.684883	-0.386165
1	1.777811	-0.159004	-0.323672
1	-1.557288	-1.402810	-0.993785
1	-1.836049	-0.742338	0.615978
1	-1.463130	-3.136287	1.522018
1	0.775331	-6.918006	-3.069615
1	-0.668307	-6.036259	-2.563339
1	0.724991	-6.454387	-0.658102
1	0.604214	-4.702221	-0.962714
1	3.222846	-7.856663	-0.523909
1	4.445831	-8.271786	1.618852
1	4.312747	-4.055895	2.453611
1	4.979766	-6.344138	3.109985
1	2.048417	-3.239319	-0.331536
1	3.724005	-2.856787	-0.574414
1	-0.259139	-1.396742	2.273996
1	0.963336	-0.232002	1.804198
1	-2.748536	-1.696863	2.487366
1	-4.477287	-0.551561	3.793230
1	-7.493470	-2.002484	1.115604
1	-5.778245	-3.095188	-0.237182
1	-8.553575	-1.952432	3.108019
1	-8.018912	1.372596	4.858501
1	-9.743632	2.525422	6.164441
1	-12.500739	-0.696179	5.293627
1	-10.757645	-1.812890	4.007142
1	-12.866563	3.277409	7.742905
1	-11.160531	2.849868	7.952583
1	-11.692423	3.704085	6.487523
1	-14.202979	1.713175	7.325472
1	-14.067556	0.930847	5.741970
1	-13.528508	0.079448	7.206027
1	1.371815	-0.749188	-4.649418
1	1.184354	-1.534441	-2.268545
1	-4.038490	6.855179	-4.486845
1	-4.889359	9.131778	-4.682424
1	-1.009575	10.645603	-3.505520
1	-0.191047	8.341268	-3.319529
1	-2.320473	5.274603	-4.003246

1	-5.053571	12.707938	-4.635037
1	-5.127402	11.204764	-5.566266
1	-5.573145	11.207362	-3.845664
1	-3.173628	13.441407	-4.056061
1	-2.309287	12.481151	-2.841824
1	-1.728163	12.533139	-4.520843
1	-0.236373	-4.022881	-5.400346
1	-1.141928	-5.405194	-4.785330
1	-1.032919	1.344331	-2.269349
1	-1.819505	3.637251	-2.488738
1	2.009285	4.843013	-3.994740
1	2.838464	2.534212	-3.738142



L_9 + Zn(II)

Table 6. Atomic numbers and the optimized X, Y, Z Cartesian parameters in Å unit for Zn^{II} complex of L_9

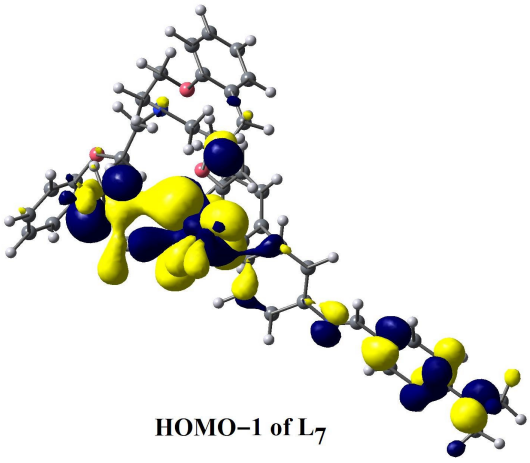
Atomic No	X	Y	Z
30	0.147224	0.415511	-0.034687
8	2.766314	1.046272	1.883504
8	-0.755890	-0.784269	3.282932
8	2.039300	-3.808103	0.557158
7	2.067931	-1.826141	2.948043
7	2.025231	0.934196	-1.022551
7	-0.766236	0.345410	-1.880106
7	-1.427692	1.609229	0.714827
7	-1.255812	-2.164889	-0.352242
7	11.783690	-6.231246	-1.533417
7	-6.642562	-3.772103	-1.309592
7	6.865000	-2.008810	-1.483665

7	-0.232862	13.548394	-1.122252
7	-13.019958	-4.940550	-1.283341
7	-0.511543	7.222333	0.250827
6	3.381298	-1.173180	2.806253
6	3.458102	0.338821	2.936505
6	3.223915	2.336437	1.672428
6	3.029099	2.929586	0.409393
6	2.184795	2.416068	-0.739158
6	1.573091	0.825838	-2.468579
6	0.123261	1.237571	-2.677040
6	-2.115925	0.962721	-1.646504
6	-2.494682	1.016246	-0.161556
6	-1.861645	1.558101	2.215593
6	-2.703991	0.421403	2.719172
6	-4.099272	0.551983	2.754998
6	-4.909751	-0.400790	3.369267
6	-4.315060	-1.502832	3.982382
6	-2.927261	-1.657433	3.974095
6	-2.122283	-0.703001	3.340203
6	-0.113376	-1.697669	4.187913
6	1.377649	-1.410092	4.178110
6	2.251443	-3.292516	2.976483
6	2.855559	-3.941963	1.730207
6	1.067179	-4.779244	0.361293
6	1.448658	-6.089789	0.060915
6	0.476303	-7.061110	-0.164548
6	-0.876690	-6.722383	-0.088230
6	-1.249908	-5.412276	0.205805
6	-0.288609	-4.412055	0.429632
6	-0.670309	-2.986344	0.767667
6	3.310034	0.196677	-0.968576
6	3.306744	-1.173752	-0.721094
6	4.504365	0.815048	-1.368395
6	4.471185	-1.925608	-0.872619
6	-0.401902	-2.142849	-1.544084
6	-0.817689	-1.026849	-2.499657
6	5.667332	0.068662	-1.507240
6	7.210918	-2.994320	-0.722792
6	8.377758	-3.813237	-0.947641
6	9.226006	-3.622516	-2.061020
6	8.709822	-4.839141	-0.041437
6	10.339958	-4.410770	-2.258475
6	5.683968	-1.319360	-1.262407
6	9.821968	-5.639471	-0.223436
6	10.677583	-5.449279	-1.342513
6	12.651817	-6.014464	-2.685690

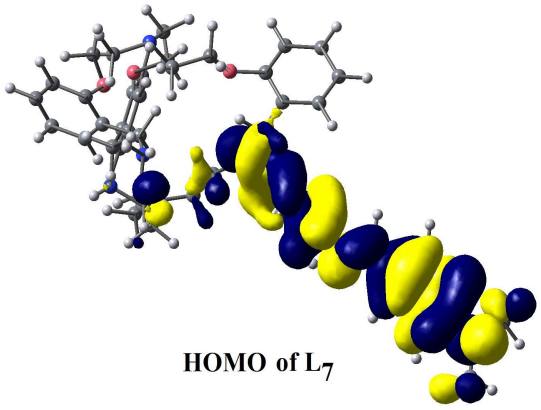
6	12.113982	-7.282590	-0.578535
6	-2.637614	-2.540185	-0.644259
6	-3.039781	-3.180157	-1.831890
6	-3.621834	-2.305011	0.327878
6	-4.363605	-3.559425	-2.028814
6	-4.945557	-2.685740	0.132998
6	-5.356640	-3.314829	-1.061033
6	-7.672089	-3.126858	-0.866762
6	-9.029388	-3.599840	-0.994627
6	-10.099642	-2.818769	-0.515843
6	-9.341313	-4.845927	-1.581340
6	-11.411593	-3.246091	-0.604897
6	-10.643795	-5.288043	-1.679731
6	-11.727196	-4.501892	-1.191136
6	-13.320230	-6.232831	-1.888809
6	-14.111981	-4.120729	-0.773032
6	-1.186960	3.054936	0.459207
6	-2.051678	3.860640	-0.296649
6	-0.143299	3.679625	1.161127
6	-0.765960	5.864567	0.268286
6	-0.746282	7.925386	-0.813289
6	-0.715202	11.413005	-2.179794
6	-0.357020	12.190466	-1.043539
6	0.124194	14.328096	0.058727
6	-0.467358	14.237721	-2.386423
6	-0.610774	9.356232	-0.872347
6	-0.256382	10.127184	0.258358
6	-0.835210	10.040319	-2.085417
6	-0.132951	11.497311	0.183006
6	-1.837732	5.234214	-0.399546
6	0.057694	5.048531	1.075517
6	3.883525	3.056836	2.680455
6	4.378398	4.337716	2.444457
6	3.555453	4.213860	0.198422
6	4.227316	4.921324	1.190348
1	3.791628	-1.438310	1.832036
1	4.088201	-1.552319	3.572162
1	3.092018	0.687341	3.907197
1	4.521490	0.594496	2.879156
1	1.730534	-0.211032	-2.767339
1	2.232794	1.437378	-3.093215
1	-0.130143	1.184864	-3.743244
1	-0.041842	2.266120	-2.349251
1	-2.884545	0.379938	-2.161467
1	-2.112405	1.959682	-2.088110
1	-3.431966	1.571031	-0.052671

1	-2.681757	0.008632	0.204573
1	-2.419011	2.485611	2.360441
1	-0.935157	1.623183	2.783759
1	-4.554232	1.438029	2.318731
1	-5.986737	-0.269972	3.392793
1	-4.927226	-2.248044	4.481630
1	-2.488378	-2.517954	4.464293
1	-0.341840	-2.727661	3.895295
1	-0.504550	-1.533692	5.198941
1	1.476619	-0.331382	4.302026
1	1.823350	-1.884019	5.072873
1	1.280316	-3.762746	3.157066
1	2.900513	-3.578598	3.828856
1	3.822580	-3.507676	1.471594
1	3.014840	-5.003203	1.951272
1	-1.416511	-2.974276	1.562750
1	0.204395	-2.450019	1.138568
1	2.504401	-6.336103	-0.008926
1	-2.304493	-5.163886	0.273375
1	-1.639899	-7.476393	-0.254532
1	0.775177	-8.077837	-0.401833
1	-1.830320	-1.201252	-2.864249
1	-0.157725	-1.047441	-3.371373
1	0.632612	-1.995375	-1.217483
1	-0.399526	-3.093778	-2.093896
1	2.408370	-1.685794	-0.391478
1	4.545345	1.876587	-1.581972
1	4.425041	-3.000066	-0.727148
1	6.590305	0.546157	-1.819764
1	6.622193	-3.245337	0.175503
1	8.985697	-2.833430	-2.766343
1	8.076733	-5.009272	0.827471
1	10.963972	-4.229758	-3.124715
1	10.036908	-6.415290	0.500387
1	13.470306	-6.733712	-2.654892
1	12.111173	-6.155283	-3.630341
1	13.084809	-5.005951	-2.680766
1	13.023169	-7.788132	-0.903929
1	12.292007	-6.874659	0.425049
1	11.314026	-8.031097	-0.511279
1	-2.329051	-3.433031	-2.610729
1	-3.348908	-1.845386	1.269870
1	-4.654556	-4.068688	-2.942367
1	-5.662591	-2.523191	0.931534
1	-7.558222	-2.145218	-0.378475
1	-9.891929	-1.851734	-0.061613

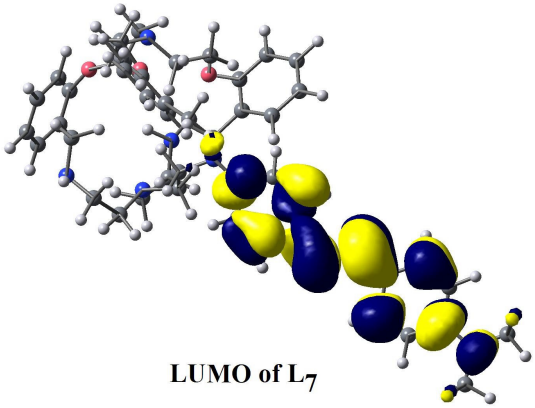
1	-8.529294	-5.459006	-1.959362
1	-12.198630	-2.608235	-0.222174
1	-10.835043	-6.251226	-2.136705
1	-12.845818	-7.056212	-1.339436
1	-14.398412	-6.392747	-1.871622
1	-12.987286	-6.276165	-2.933724
1	-15.054972	-4.646016	-0.924878
1	-14.001210	-3.925639	0.301592
1	-14.171080	-3.157111	-1.295484
1	-2.927032	3.451496	-0.788046
1	0.518990	3.095027	1.793201
1	-2.543800	5.833667	-0.965611
1	0.862483	5.520216	1.628847
1	-1.053371	7.438621	-1.752896
1	-0.081630	9.616348	1.199948
1	-1.113286	9.474612	-2.972510
1	0.136723	12.048462	1.075354
1	-0.901670	11.891998	-3.132596
1	1.098578	14.024219	0.461196
1	0.185755	15.381248	-0.214808
1	-0.627434	14.225452	0.851549
1	0.225340	13.893724	-3.165021
1	-1.494154	14.087770	-2.743593
1	-0.312553	15.307221	-2.244290
1	1.176115	2.821062	-0.633651
1	2.588060	2.876036	-1.648295
1	4.014496	2.625151	3.664176
1	4.886604	4.868132	3.243942
1	3.422466	4.674579	-0.777616
1	4.624520	5.909467	0.982657



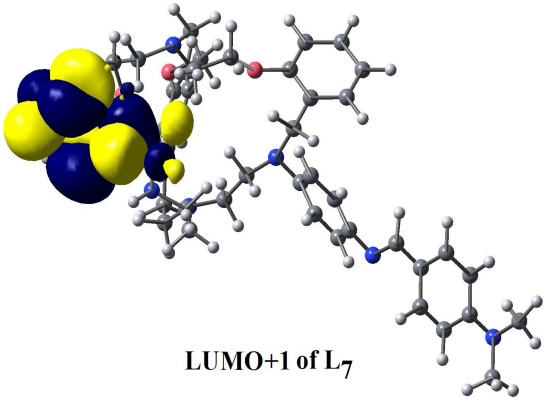
HOMO−1 of L_7



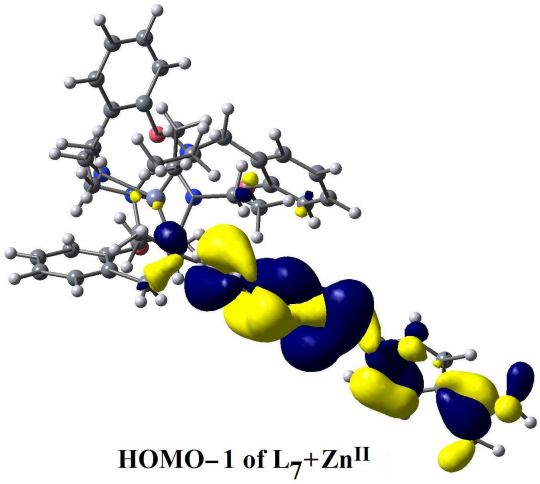
HOMO of L_7



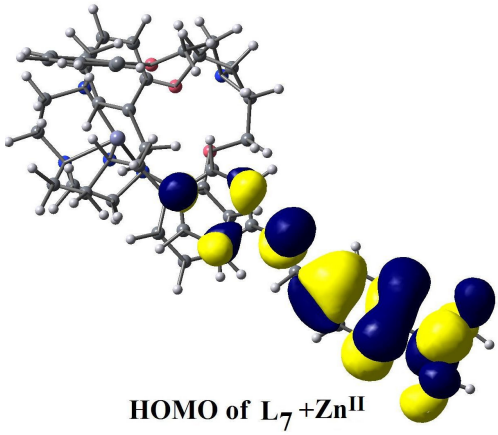
LUMO of L_7



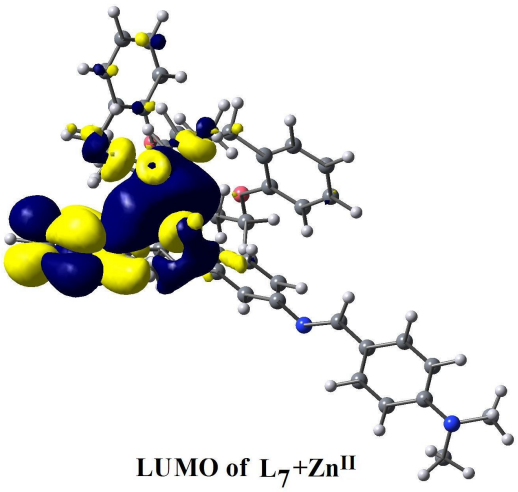
LUMO+1 of L_7



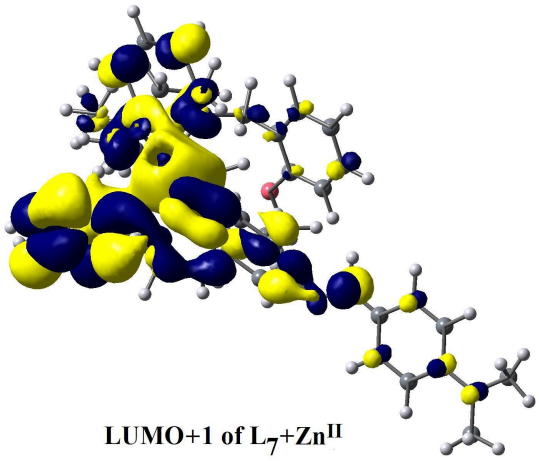
HOMO−1 of L_7+Zn^{II}



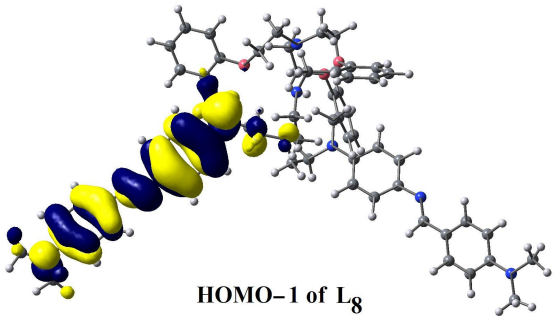
HOMO of L_7 +Zn^{II}



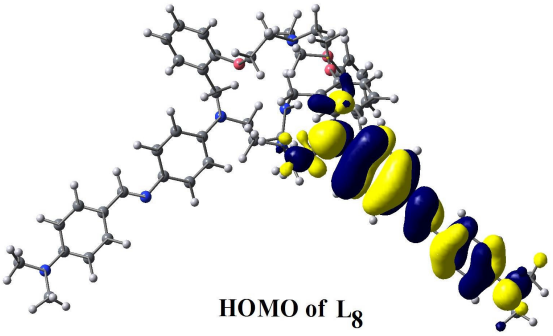
LUMO of L_7+Zn^{II}



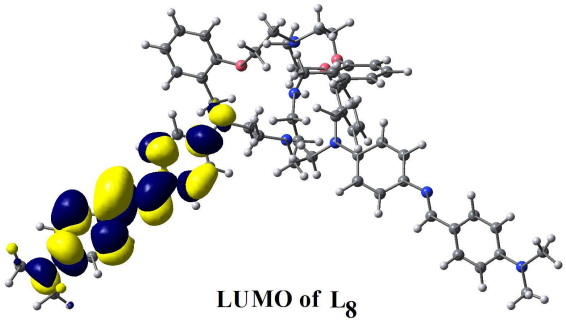
LUMO+1 of L_7+Zn^{II}



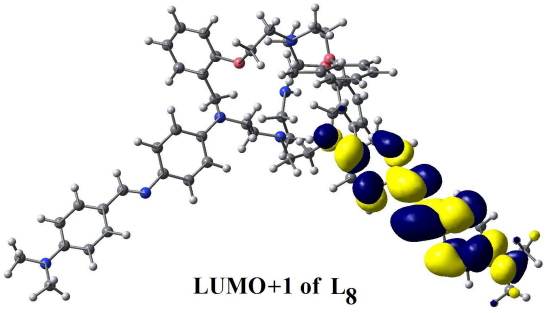
HOMO−1 of L_8



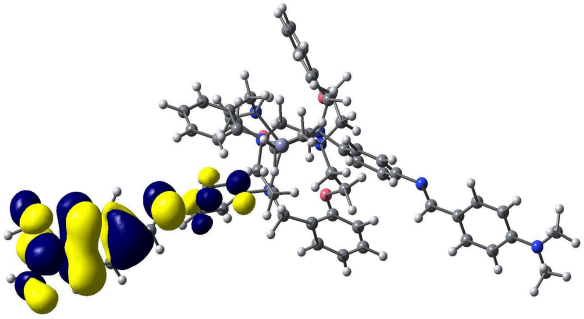
HOMO of L_8



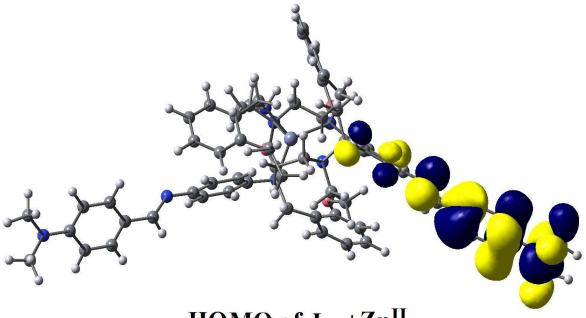
LUMO of L_8



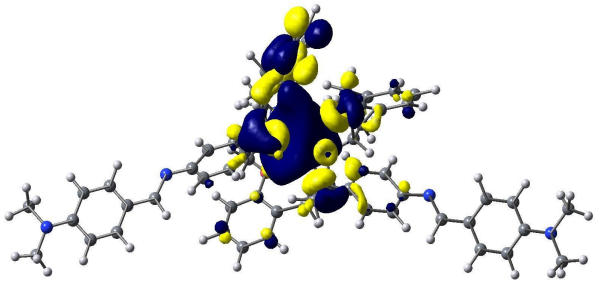
LUMO+1 of L_8



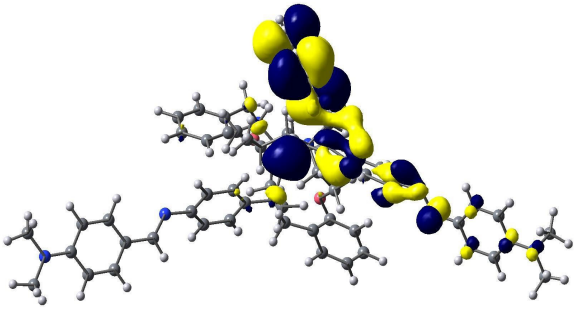
HOMO−1 of L_8+Zn^{II}



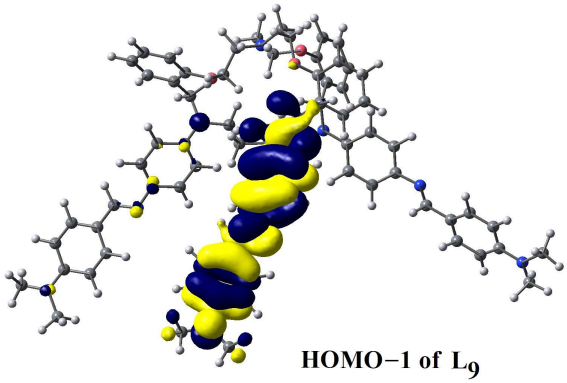
HOMO of L_8+Zn^{II}



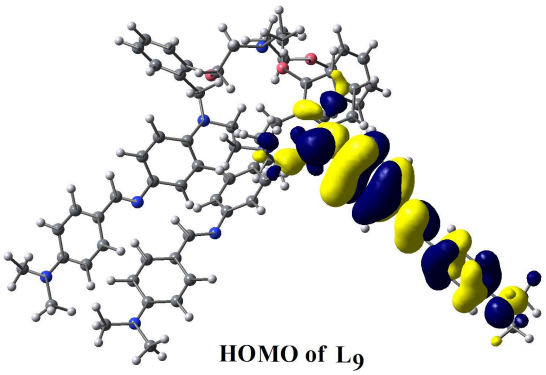
LUMO of L_8+Zn^{II}



LUMO+1 of L_8+Zn^{II}



HOMO−1 of L_9



HOMO of L_9

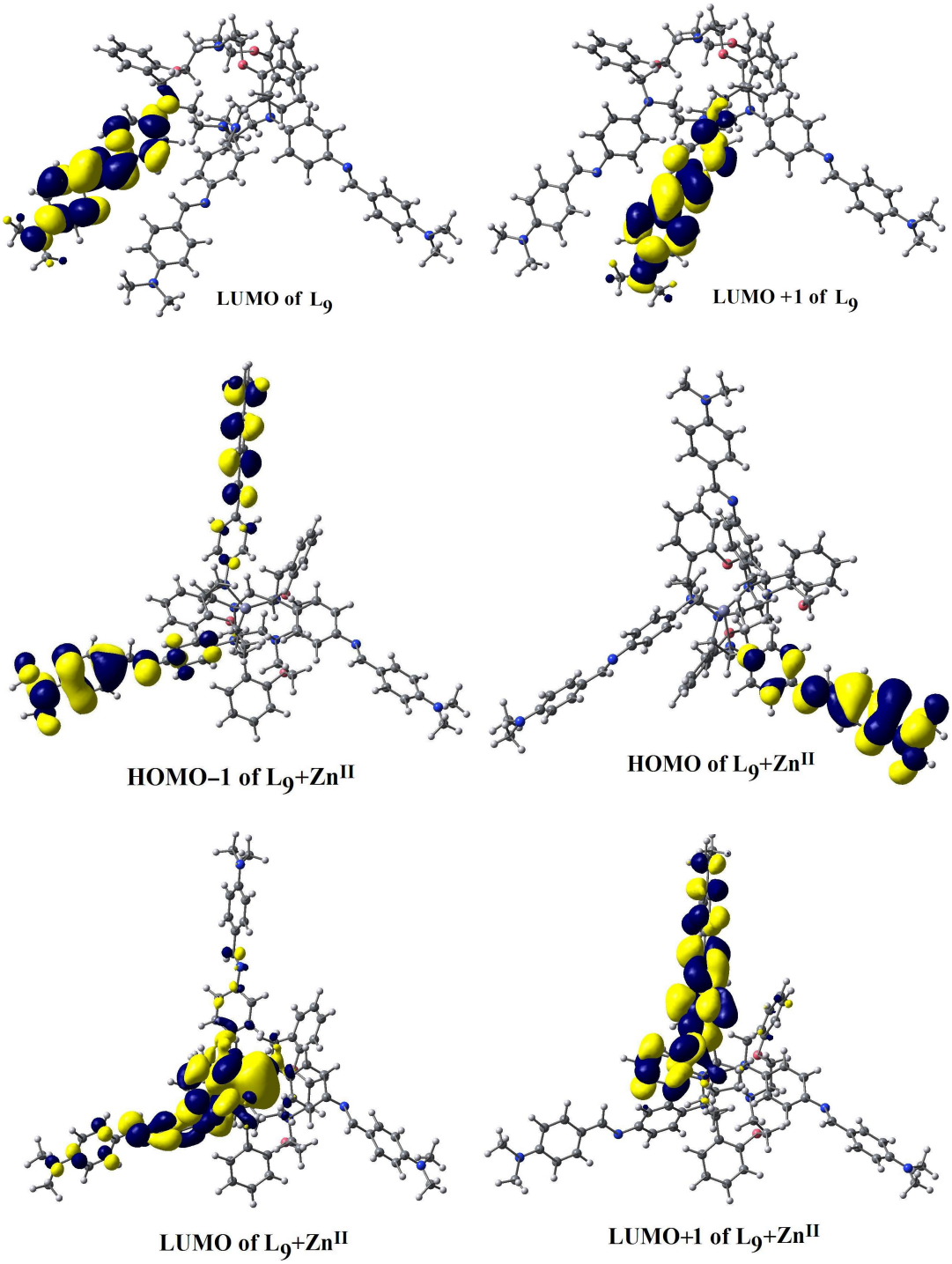


Figure S44: Contour surfaces of **HOMO–1, HOMO, LUMO** and **LUMO+1** for the chromophores $\mathbf{L_7}$ to $\mathbf{L_9}$ and their corresponding Zn^{II} complexes.

References.

[1] G. S. He, L. Yuan, N. Cheng, J. D. Bhawalkar, P. N. Prasad, L. L. Brott, S. J. Clarson, B. A. Reinhardt, *J. Opt. Soc. Am. B* **1997**, *14*, 1079.

[2] M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan, E. W. Van Stryland, *IEEE J. Quantum Electron.* **1990**, *26*, 760–769.

[3] D. S. Correa, S. L. Oliveira, L. Misoguti, S. C. Zilio, R. F. Aroca, C. J. L. Constantino, C. R. Mendonca, *J. Phys. Chem. A* **2006**, *110*, 6433–6438.

[4] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.