Phenylene-diimine capped conjugate of lower rim 1, 3-calix[4]arene as molecular receptor for Mg^{2+} *via* arm conformational changes followed by aggregation and mimicking the species by molecular mechanics

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Supporting Information

SI 01 Characterization of precursors

(a) Characterization of 2

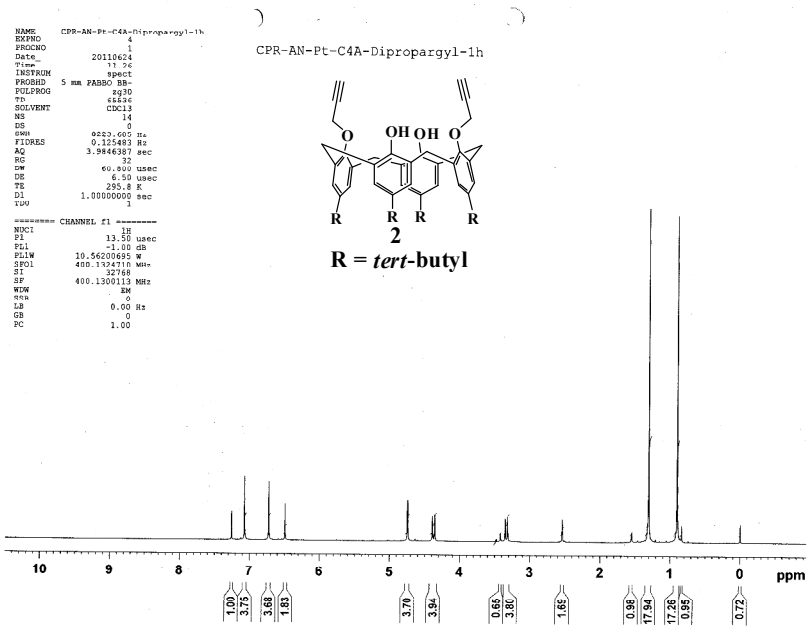


Figure SI01 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 2.

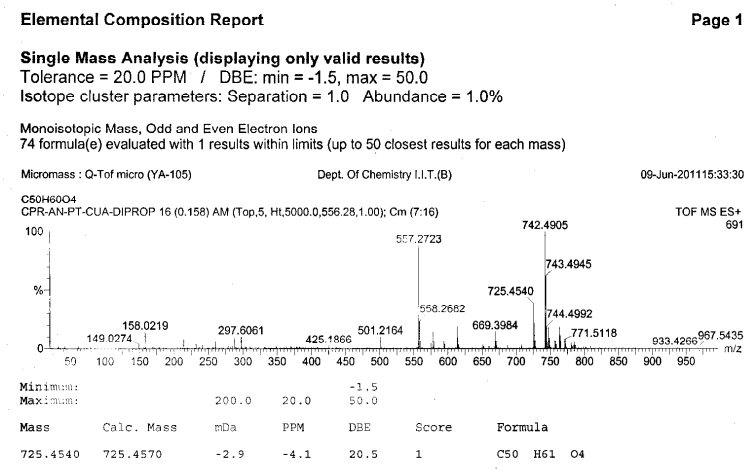


Figure SI02 HRMS spectrum of 2.

(b) Characterization of 3

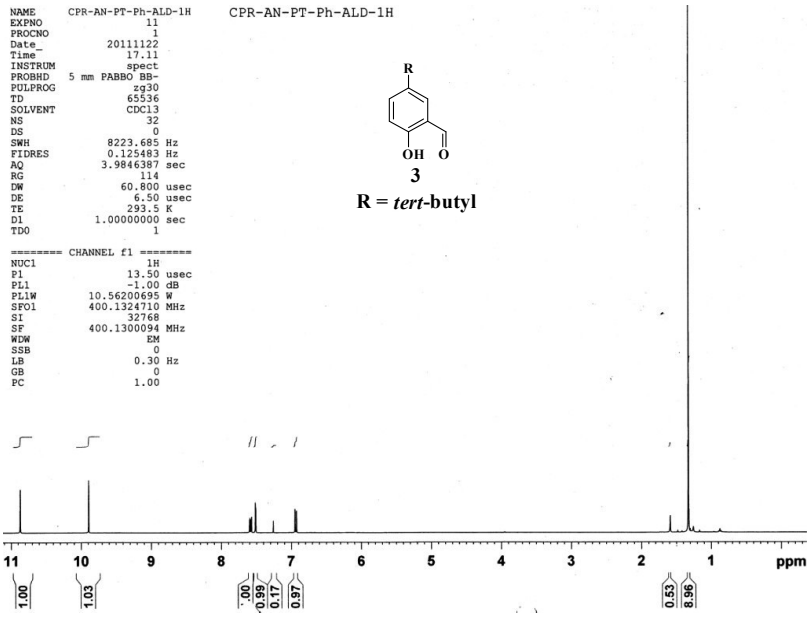


Figure SI03 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 3.

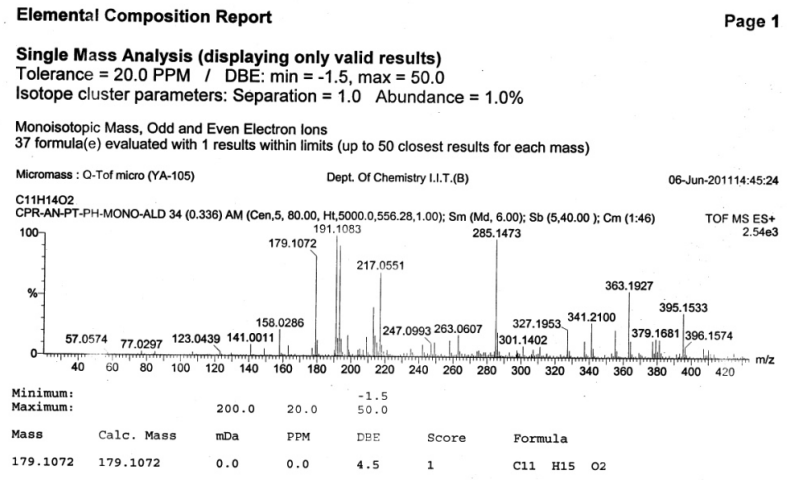


Figure SI04 HRMS spectrum of 3.

(c) Characterization of 4

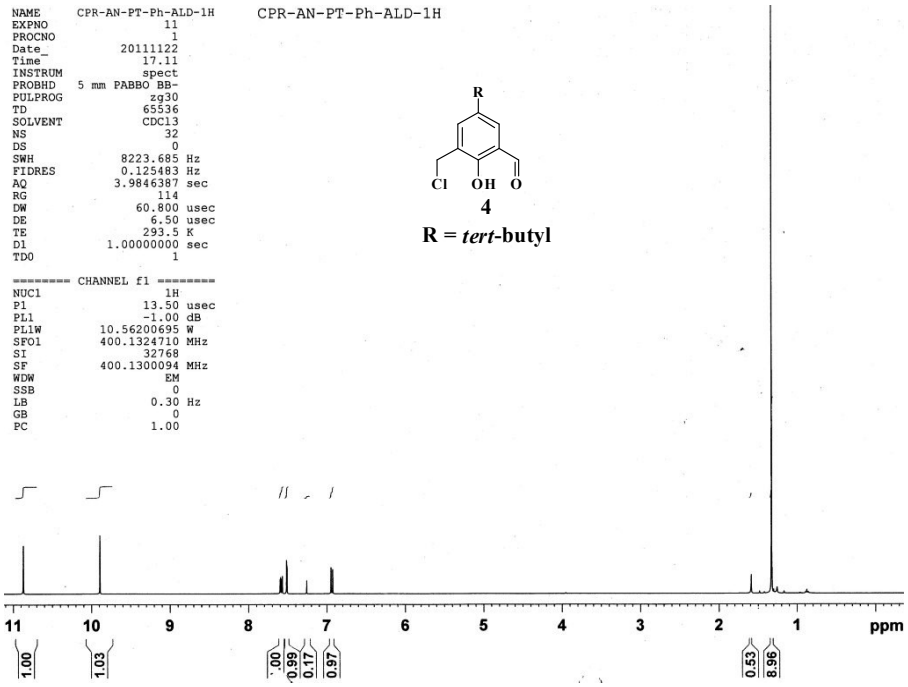


Figure SI05 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 4

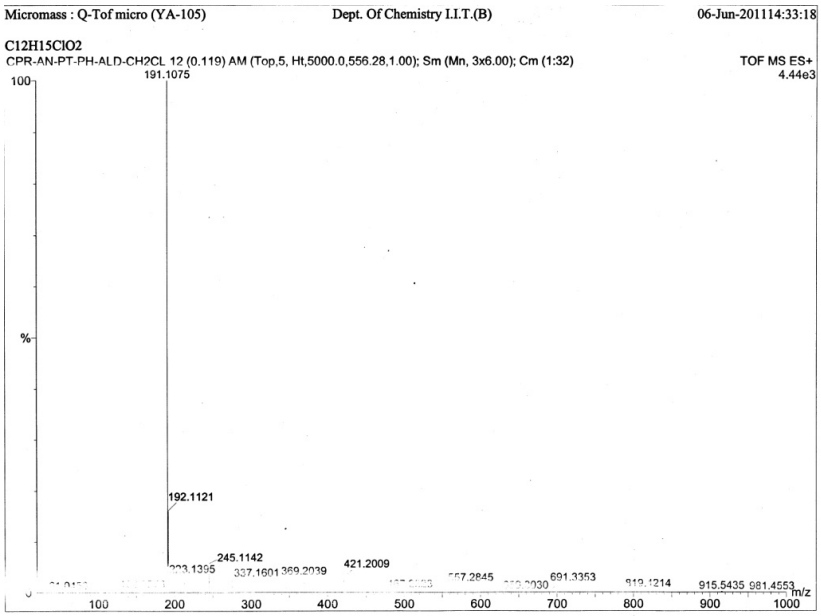


Figure SI06 ESI MS spectrum of 4.

(d) **Characterization of 5**

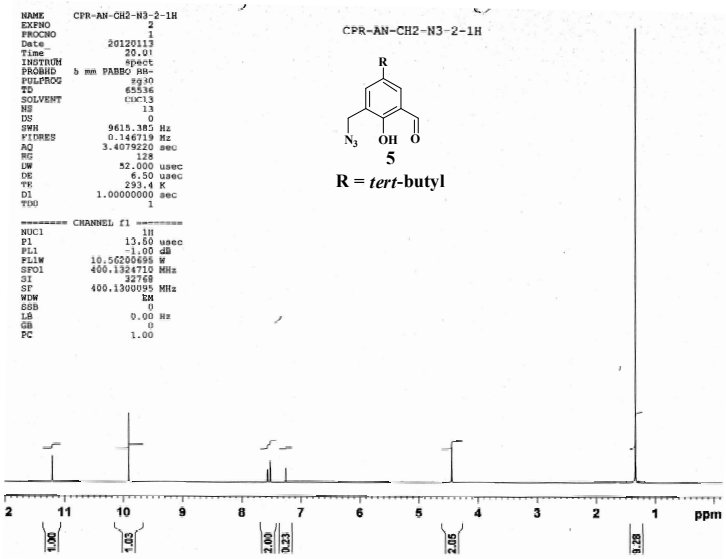


Figure SI07 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 5.

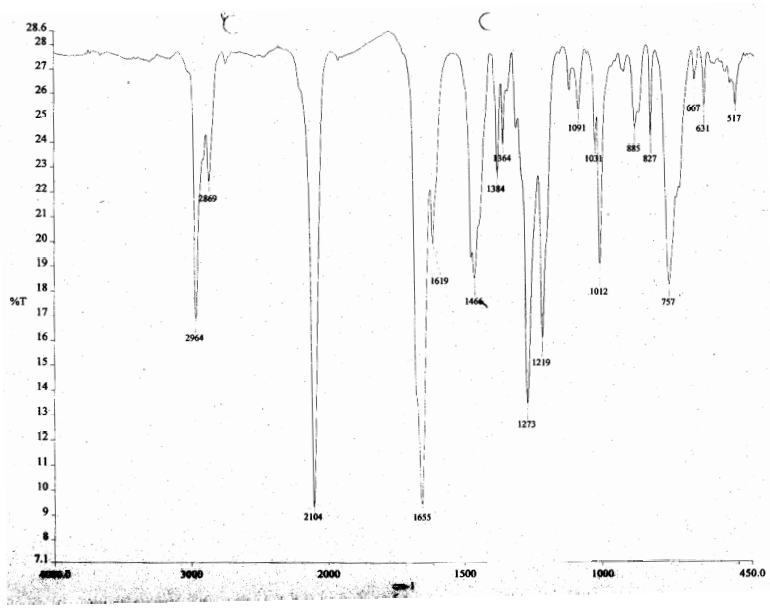


Figure SI08 FTIR spectrum of 5.

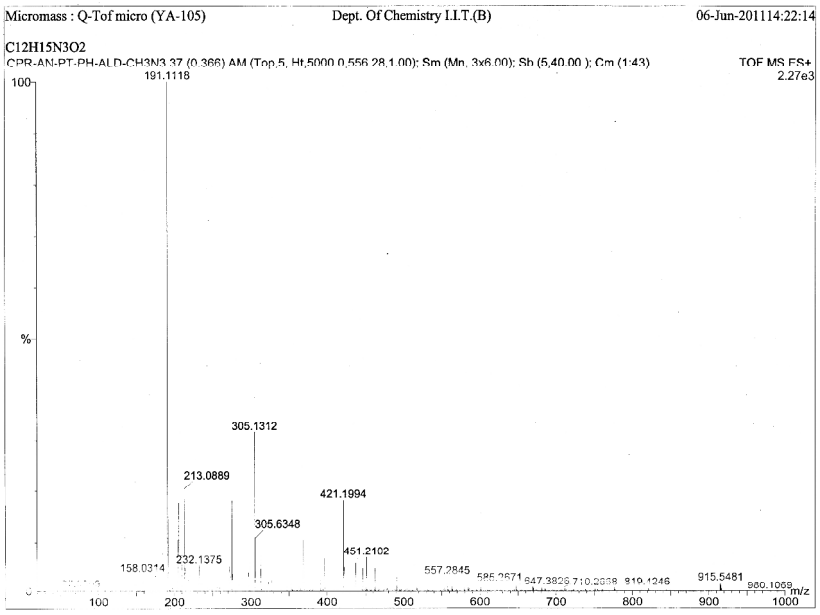


Figure SI09 ESI MS spectrum of 5.

(e) Characterization of L′

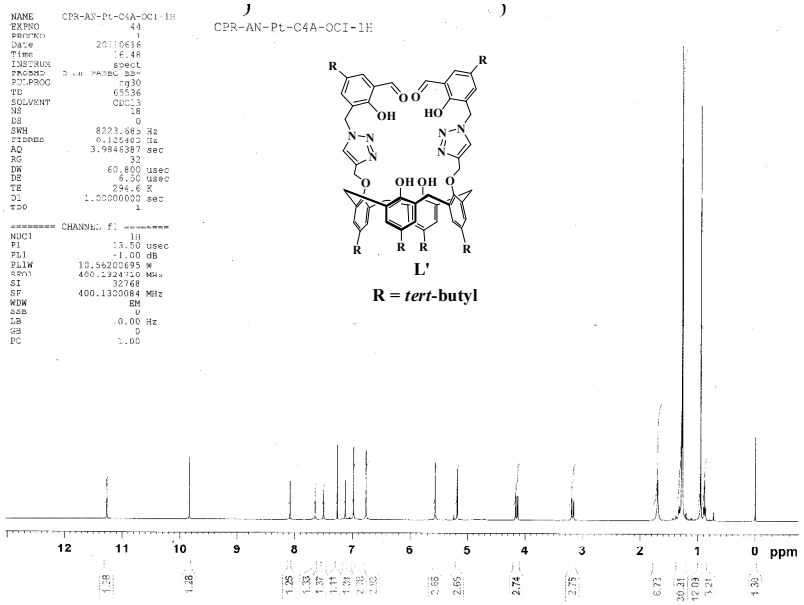


Figure SI10 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of L′.

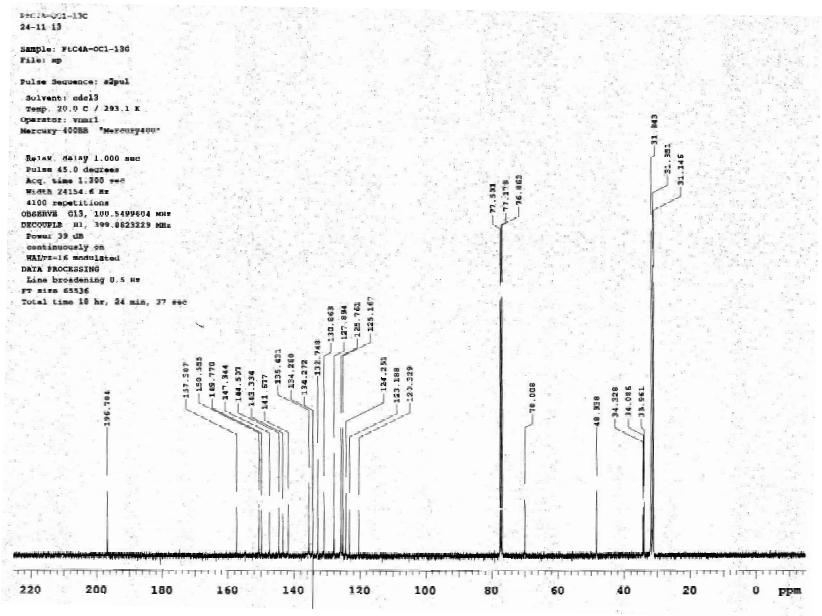


Figure SI11 ^{13}C NMR spectrum ($CDCl_3$, 400 MHz) of L′.

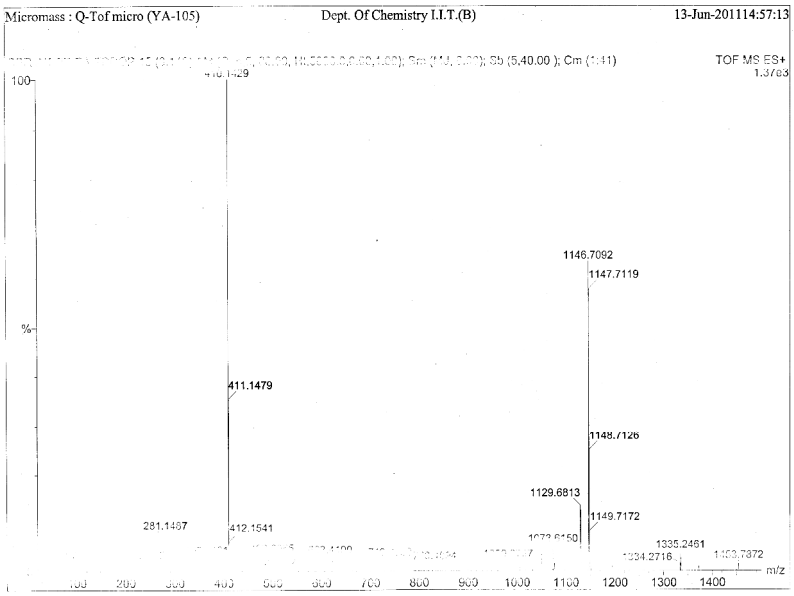


Figure SI12 ESI MS spectrum of L′.

(d) Characterization of L

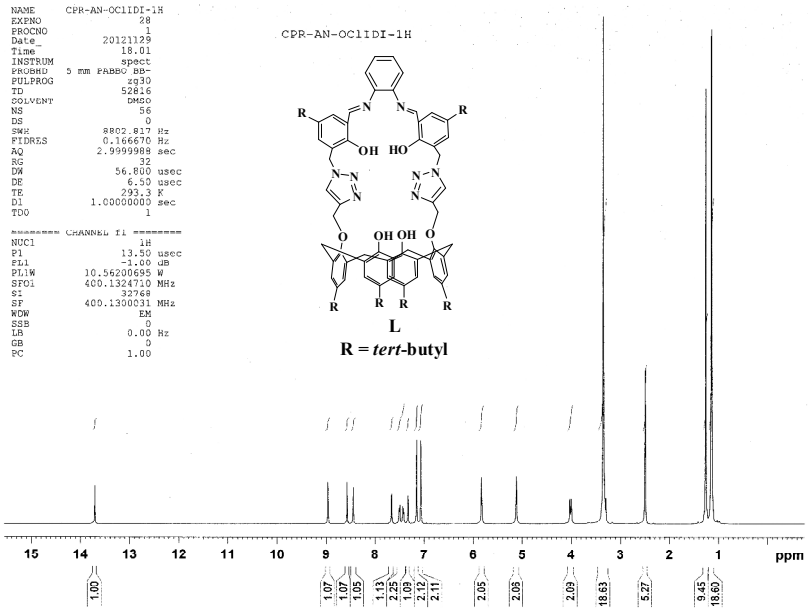


Figure SI13 ^{1}H NMR spectrum (DMSO-d^{6}, 400 MHz) of **L**.

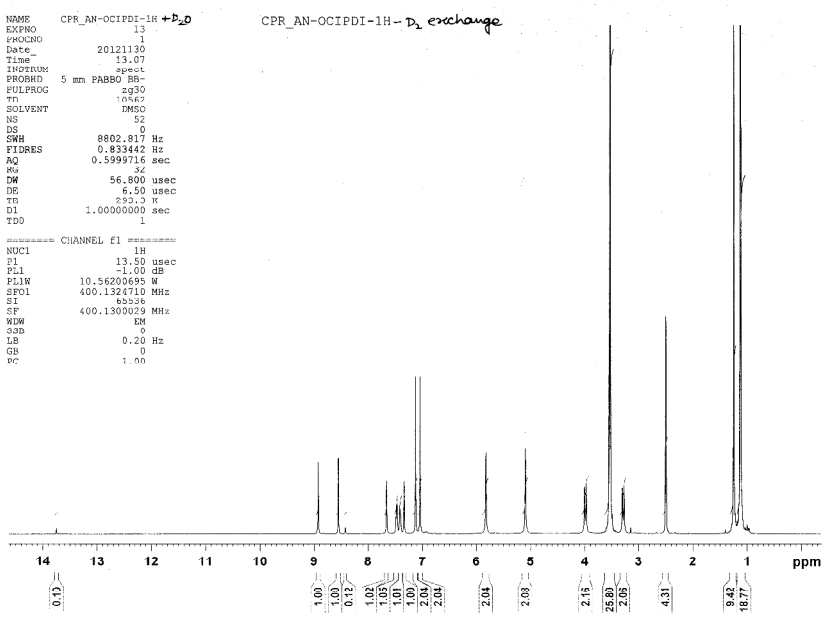


Figure SI14 ^{1}H NMR spectrum (DMSO-d^{6} and 2 dropes of D_2O, 400 MHz) of **L**.

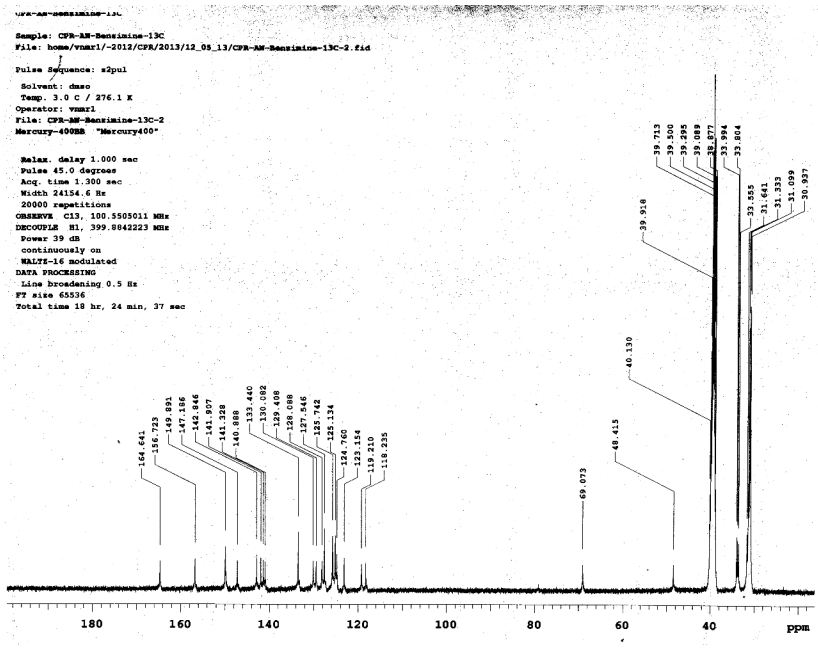


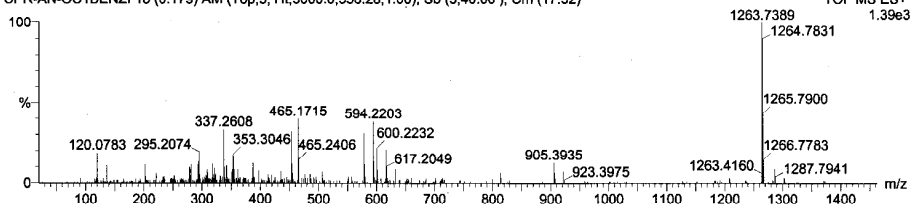
Figure SI15 ^{13}C NMR spectrum (DMSO-d^6, 400 MHz) of **L**.

Elemental Composition Report **Page 1**

Single Mass Analysis (displaying only valid results)
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
43 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Micromass : Q-Tof micro (YA-105) Dept. Of Chemistry I.I.T.(B) 04-Nov-201115:32:05
C80H94N8O6 Pt C4A
CPR-AN-OC1BENZI 18 (0.179) AM (Top,5, Ht,5000.0,556.28,1.00); Sb (5,40.00); Cm (17:32) TOF MS ES+
1.39e3



Minimum:				-1.5		
Maximum:		200.0	20.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
1263.7389	1263.7375	1.4	1.1	37.5	1	C80 H95 N8 O6

Figure SI16 HRMS spectrum of **L**.

SI 02 Estimation of association constant

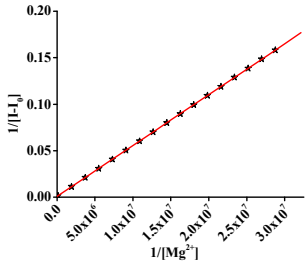


Figure SI17 The binding constant of **L** with Mg^{2+} has been derived by Benesi–Hildebrand equation in acetonitrile.

SI 03 Experiment determining the minimum detection limit

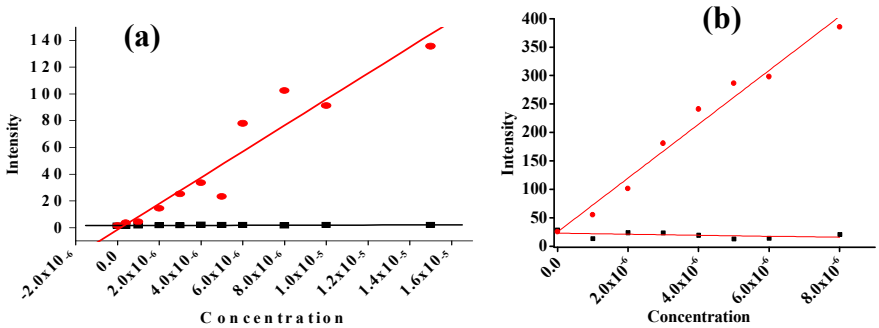


Figure SI18 Detection of minimum concentration of **L** for sensing the Mg^{2+} in (a) acetonitrile and (b) in presence of blood serum.

SI 04 Quantum yield calculation

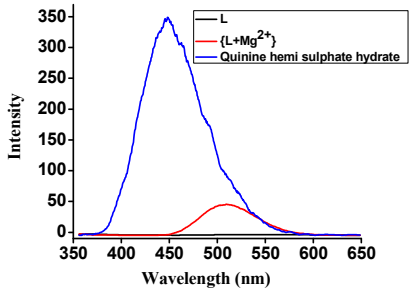


Figure SI19 Calculation of quantum yield of **L** in presence of Mg^{2+} and quinine hemi sulphate hydrate as reference.

SI 05 Fluorescence studies of L with metal ions in acetonitrile

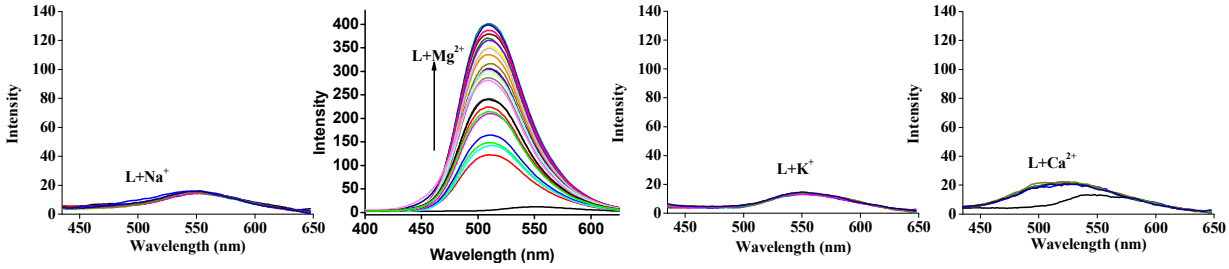


Figure SI20 Fluorescence spectra obtained during the titration of **L** with Na^+, Mg^{2+}, K^+, and Ca^{2+} ions respectively in acetonitrile.

SI 06 Competitive metal ion titration

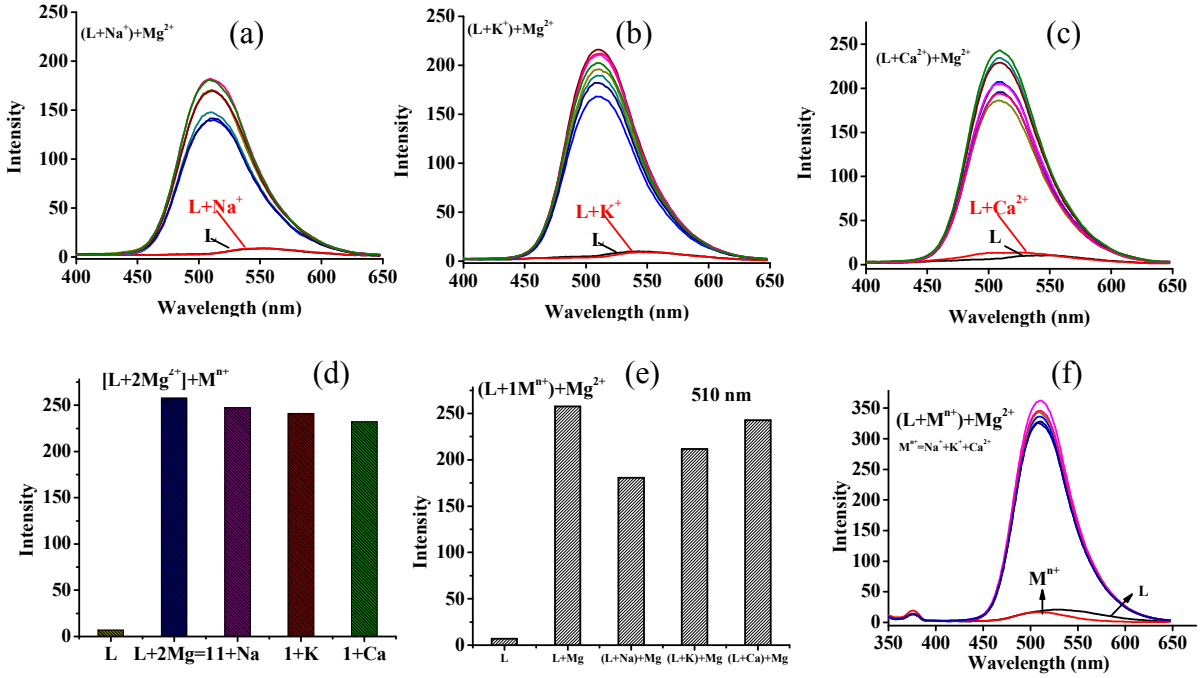


Figure SI21 Fluorescence spectral traces for the titration of [**L**+M^{n+}] in the ratio 1:1 followed by incremental addition of Mg^{2+} metal ion in acetonitrile (a,b, c and e); Histogram shows intensity vs. metal ion upon titration of [**L** +2Mg^{2+}] with M^{n+} (d); Spectral traces of titration of {**L**+M^{n+}}+Mg^{2+} (f); where M^{n+}= Na^+, K^+ and Ca^{2+}.

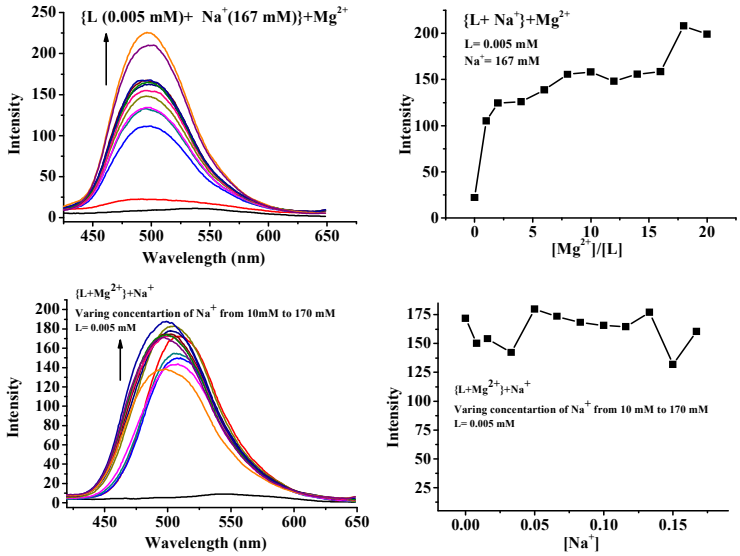


Figure SI22 Fluorescence spectral traces for the titration of **L** with Na^+ followed by Mg^{2+} and vice versa in acetonitrile where [Na^+] is 167 mM.

SI 07 Absorption studies of L with metal ions in acetonitrile

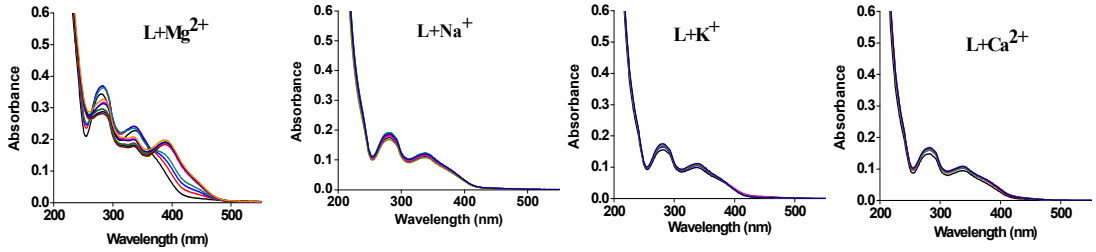


Figure SI23 Absorption spectra obtained during the titration of **L** with Mg^{2+}, Na^+, K^+ and Ca^{2+} ions respectively in acetonitrile.

SI 08 Absorption studies of L with $Mg(CH_3COO)_2$ in acetonitrile

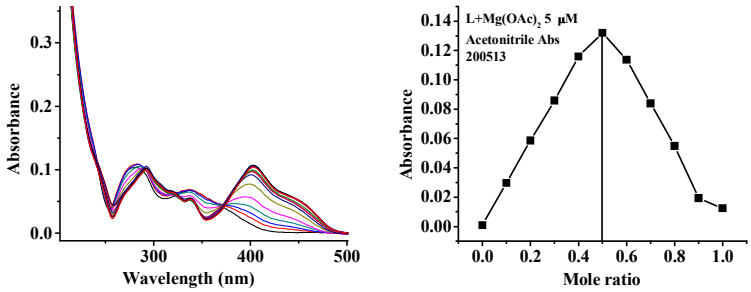


Figure SI24 Absorption titration of **L** with $Mg(CH_3COO)_2$ in acetonitrile: (a) Absorption spectra obtained during the titration of **L** with Mg^{2+}. (b) Job's plot obtained from the absorption titration data of **L** with $Mg(CH_3COO)_2$.

SI 09 ^{1}H NMR data of L with $Mg(CH_3COO)_2$

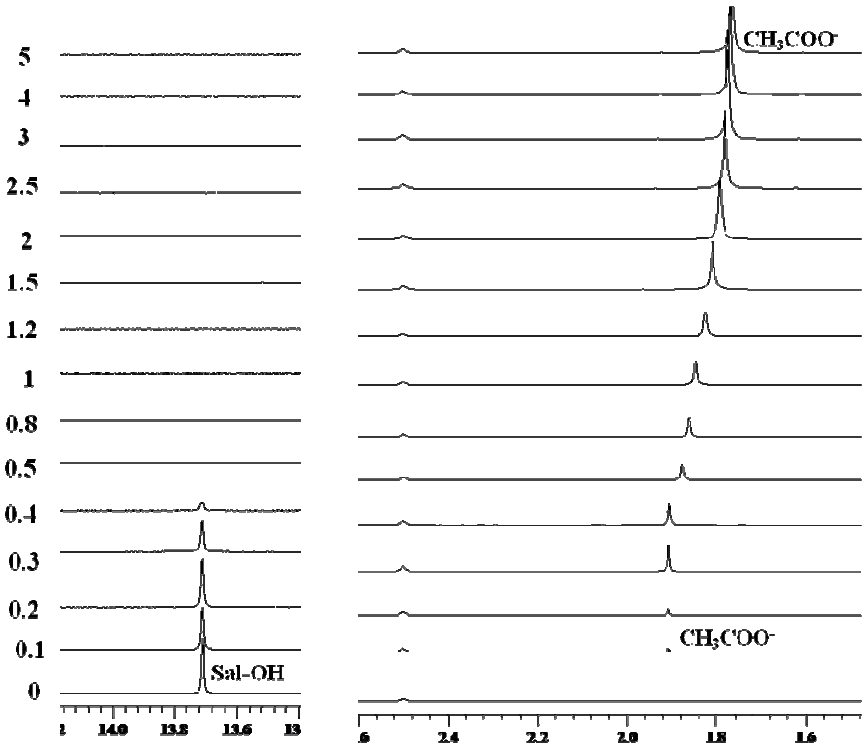


Figure SI25 ^{1}H NMR titration in DMSO-d^6 at 400 MHz of **L** with $Mg(CH_3COO)_2$ in increasing amount of concentration of Mg^{2+} from down to up. Mole ratios are mentioned at left side of each spectrum. Herein the changes in chemical shift of Sal-O**H** and C**H**$_3$COO$^-$ are shown.

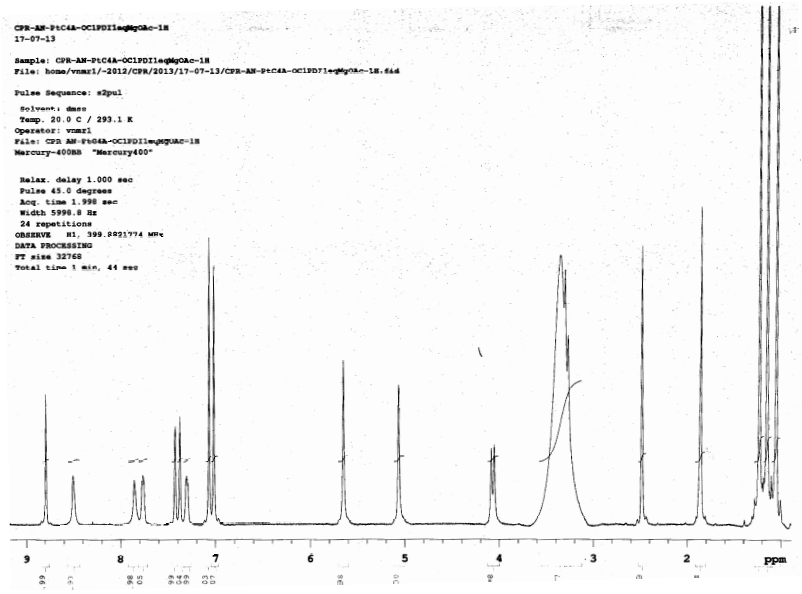


Figure SI26 ^{1}H NMR spectrum (DMSO-d^6, 400 MHz) of L + 1$Mg(CH_3COO)_2$

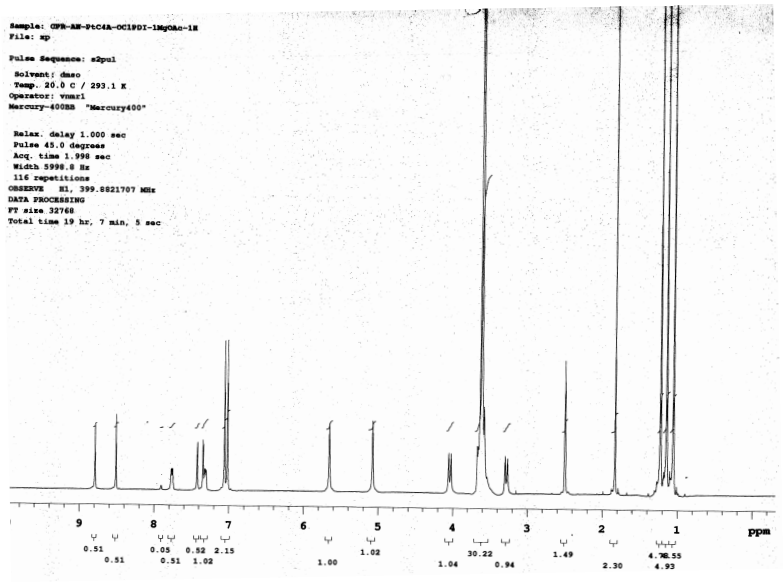


Figure SI27 ^{1}H NMR spectrum (DMSO-d^{6} and 2 drops of D_2O, 400 MHz) of L + 1Mg$(CH_3COO)_2$.

SI 10 ESI MS titration of L with $Mg(CH_3COO)_2$ in acetonitrile

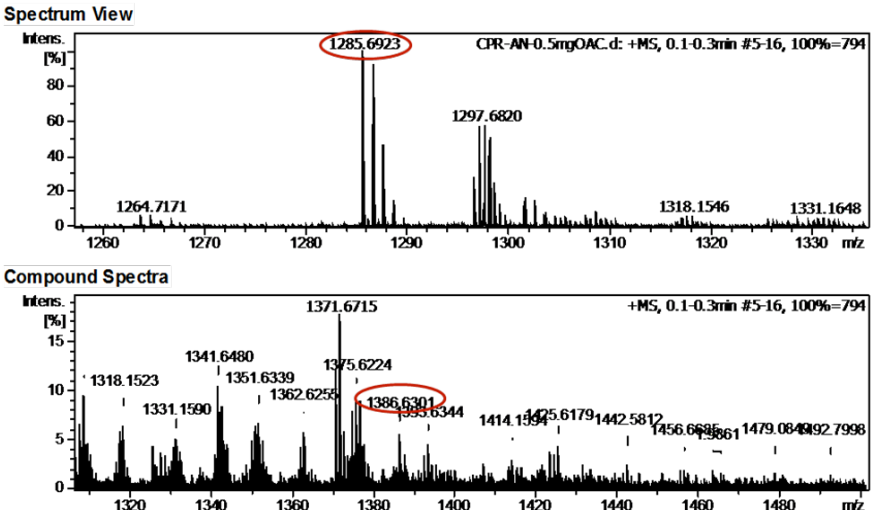


Figure SI28 ESI MS spectrum of **L** with 0.5 equivalent of $Mg(CH_3COO)_2$.

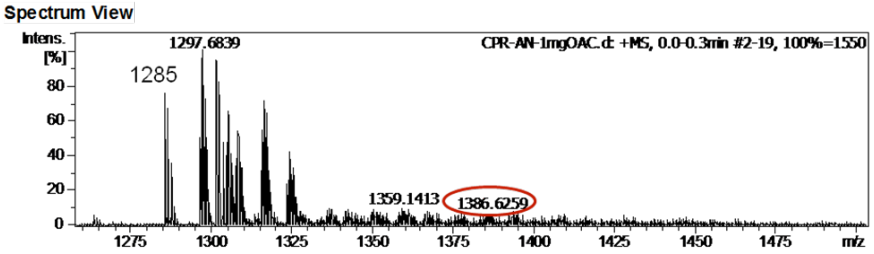


Figure SI29 ESI MS spectrum of **L** with 1 equivalent of $Mg(CH_3COO)_2$.

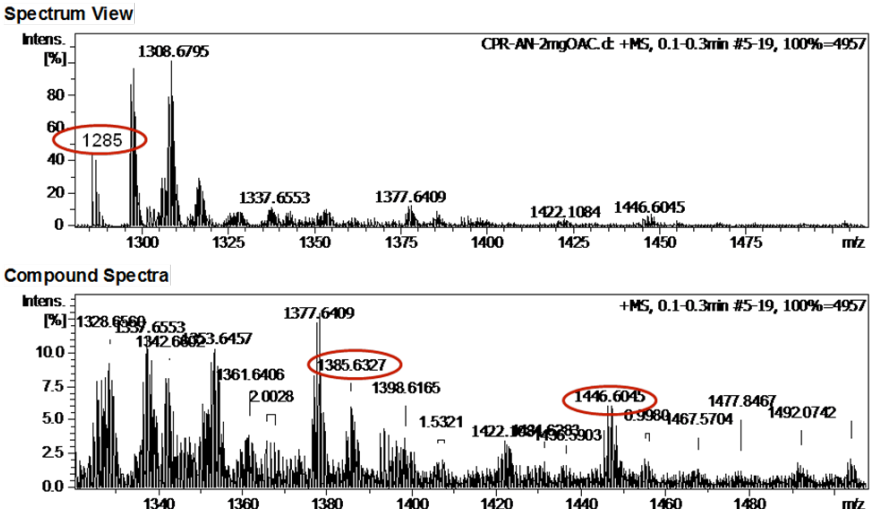


Figure SI30 ESI MS spectrum of **L** with 2 equivalent of $Mg(CH_3COO)_2$.

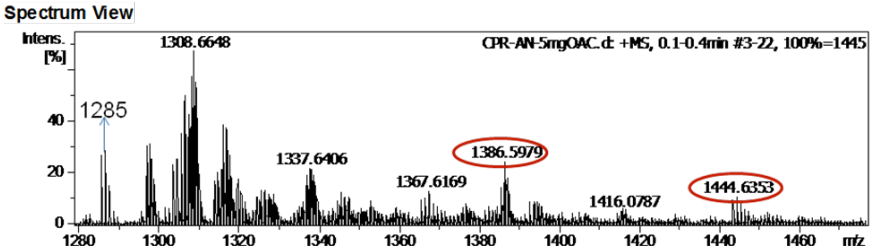


Figure SI31 ESI MS spectrum of **L** with 5 equivalent of $Mg(CH_3COO)_2$.

SI 11 Table showing distance between protons in free L and in complex

	L		$[\mathbf{L}^{2-}.Mg^{2+}.(CH_3CO_2H)_2]$	
	Arm1	Arm2	Arm1	Arm2
a□-d□	2.461	2.489	2.432	2.387
a□-b□	2.236	2.627	2.280	2.232
b□-d□	4.570	4.880	4.596	4.476
g□-h□	2.247	5.338	4.235	4.002
g□-h′*	4.312	6.657	7.182	4.251

SI 12 Cartesian coordinates for MM+ minimized structure of L

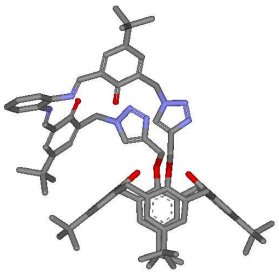


Figure SI32 MM minimized structures of **L**.

Z	Coordinates			Z	Coordinates		
	x	y	z		x	y	z
6	-3.792	-1.359	3.627	6	3.843	-0.509	3.975
6	-3.266	-4.069	0.966	6	3.676	0.247	5.219
8	-0.411	-3.664	2.229	6	3.933	0.2	2.691
6	-5.001	-0.48	3.96	6	3.825	1.666	2.649
6	-5.845	-0.257	2.666	1	-0.73	6.064	3.532
6	-5.871	-1.189	5.043	1	0.882	-1.88	3.186
6	-4.595	0.923	4.508	1	0.288	-1.059	4.628
6	2.536	5.237	-0.504	1	-4.961	-3.055	2.878
6	1.973	5.531	-1.836	1	-2.206	-0.065	4.422
6	2.416	4.69	-2.964	1	-6.271	-1.197	2.317
6	3.434	4.094	-0.282	1	-5.215	0.156	1.877
6	3.941	3.333	-1.44	1	-6.664	0.438	2.863
6	3.398	3.613	-2.779	1	-6.245	-2.144	4.671
6	0.886	6.601	-1.99	1	-6.725	-0.563	5.309
6	1.354	7.936	-1.33	1	-5.275	-1.371	5.939
6	0.552	6.914	-3.483	1	-3.971	1.446	3.781
6	-0.417	6.099	-1.299	1	-4.045	0.823	5.446
6	3.654	3.654	1.104	1	-5.485	1.527	4.696
8	4.954	2.438	-1.327	1	-3.935	-4.886	1.244
1	5.437	2.322	-0.531	1	-2.388	-4.508	0.502
6	3.855	2.819	-3.983	1	-2.294	-1.649	-3.549
6	0.097	-0.537	-4.11	1	2.19	5.772	0.332

6	1.438	0.06	-4.422	1	2.024	4.846	-3.925
6	1.725	1.492	-4.386	1	0.612	8.72	-1.497
7	3.101	1.587	-4.094	1	2.304	8.254	-1.764
7	3.645	0.338	-4.033	1	1.482	7.815	-0.253
7	2.666	-0.605	-4.194	1	-0.182	7.72	-3.544
7	4.048	-0.498	1.473	1	0.131	6.034	-3.973
7	3.82	2.282	1.379	1	1.453	7.225	-4.015
6	5.82	-3.469	-0.157	1	-0.75	5.172	-1.768
6	5.653	-4.462	-1.237	1	-1.208	6.845	-1.396
6	4.368	-4.458	-1.964	1	-0.242	5.915	-0.239
6	4.876	-2.355	0.007	1	3.425	4.317	1.887
6	3.812	-2.184	-0.997	1	4.919	2.592	-3.893
6	3.415	-3.351	-1.797	1	3.712	3.408	-4.891
6	6.742	-5.508	-1.493	1	-0.655	-0.078	-4.753
6	6.802	-6.491	-0.284	1	0.124	-1.61	-4.304
6	6.482	-6.338	-2.79	1	1.02	2.222	-4.127
6	8.121	-4.797	-1.664	1	6.611	-3.571	0.528
6	4.873	-1.621	1.28	1	4.082	-5.286	-2.543
8	3.224	-0.989	-1.243	1	7.558	-7.259	-0.46
1	3.558	-0.185	-0.891	1	5.833	-6.975	-0.147
6	3.675	1.712	5.189	1	7.059	-5.957	0.632
1	5.578	-6.94	-2.685	1	7.319	-7.013	-2.978
1	8.067	-4.07	-2.477	1	6.372	-5.673	-3.648
1	8.896	-5.529	-1.899	6	-3.99	-2.663	2.97
1	8.407	-4.279	-0.748	6	-1.267	-1.681	3.304
1	0.359	-5.447	2.807	6	-2.403	-0.922	3.848
1	-1.242	-5.55	2.066	6	3.784	2.42	3.91
1	1.818	-3.57	0.684	6	1.965	-3.558	-2.171
6	-3.172	-2.436	-1.063	6	-0.282	-5.038	2.024
6	-3.883	-1.713	-2.13	6	0.383	-5.265	0.694
6	-5.35	-1.639	-2.114	6	1.439	-4.4	0.169
6	-3.946	-3.171	-0.045	7	1.33	-4.469	-1.237
6	-5.417	-3.137	-0.088	7	0.312	-5.314	-1.568
6	-6.145	-2.316	-1.073	7	-0.282	-5.802	-0.435
8	-1.817	-2.385	-1.045	1	-5.836	-1.076	-2.857
6	-7.672	-2.176	-1.068	1	-5.948	-3.713	0.611
6	-8.053	-0.672	-0.905	1	-7.666	-0.083	-1.737
6	-8.247	-2.721	-2.411	1	-7.639	-0.281	0.026
6	-8.352	-2.964	0.096	1	-9.139	-0.558	-0.88
6	-3.111	-1.007	-3.222	1	-7.88	-2.136	-3.255
6	-1.18	0.485	-2.295	1	-9.338	-2.666	-2.404
6	-0.837	1.534	-1.319	1	-7.949	-3.762	-2.549
6	-1.864	2.501	-0.907	1	-7.986	-2.611	1.061
6	-2.588	0.315	-2.703	1	-8.147	-4.032	0.002
6	-3.57	1.348	-2.341	1	-9.434	-2.819	0.065

6	-3.276	2.318	-1.273	1	-3.759	-0.823	-4.081
6	0.565	1.682	-0.77	1	-1.585	3.32	-0.314
8	-0.191	-0.324	-2.76	1	-4.53	1.304	-2.764
6	-4.376	3.098	-0.549	1	-3.177	3.858	1.131
6	-4.046	3.219	0.973	1	-3.839	2.232	1.388
6	-4.476	4.52	-1.176	1	-4.89	3.657	1.511
6	-5.762	2.389	-0.664	1	-3.528	5.049	-1.065
6	0.509	0.225	1.4	1	-5.258	5.097	-0.679
6	0.341	0.158	2.862	1	-4.713	4.446	-2.238
6	0.264	1.395	3.65	1	-5.68	1.354	-0.326
6	0.551	1.542	0.736	1	-6.117	2.4	-1.695
6	0.444	2.765	1.548	1	-6.502	2.901	-0.045
6	0.182	2.712	2.997	1	1.238	0.945	-1.204
6	0.139	-1.172	3.553	1	0.937	2.669	-1.045
8	0.587	-0.938	0.709	1	0.165	1.325	4.694
6	-0.272	3.937	3.797	1	0.497	3.692	1.06
6	-1.677	3.654	4.415	1	-1.632	2.815	5.111
6	0.749	4.232	4.938	1	-2.389	3.416	3.623
6	-0.39	5.225	2.922	1	-2.036	4.531	4.956
6	-1.507	-2.932	2.558	1	0.846	3.373	5.603
6	-2.898	-3.295	2.214	1	0.418	5.089	5.527
1	0.58	5.483	2.494	1	1.726	4.46	4.511
1	5.546	-1.903	2.038	1	-1.11	5.072	2.116
1	3.606	2.255	6.085	1	3.584	-0.26	6.134
1	3.835	-1.559	4.001	1	1.909	-3.968	-3.181
1	3.857	3.467	3.909	1	1.432	-2.607	-2.154
1	-1.344	-1.929	-1.745	1	0.558	-1.776	1.176

SI 13 Cartesian coordinates for MM+ minimized structure of [L^{2-}.Mg^{2+}.$(CH_3CO_2H)_2$]

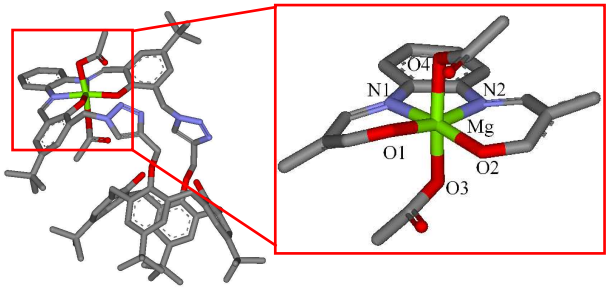


Figure SI33 MM minimized structures of [$\mathbf{L}^{2-}$.Mg^{2+}.$(CH_3CO_2H)_2$] and the binding sphere around the Mg^{2+} center.

Z				Z			
	x	y	z		x	y	z
6	5.452	0.198	1.4	8	2.3	2.021	-0.655
6	6.077	-0.707	2.378	6	2.585	4.57	4.617
6	6.944	-0.163	3.433	6	3.701	3.878	5.46
6	5.71	1.649	1.487	6	2.934	6.078	4.423
6	6.641	2.161	2.506	6	1.254	4.491	5.429
6	7.21	1.283	3.544	6	-0.181	-4.221	-6.653
8	4.648	-0.342	0.45	6	1.249	-3.975	-6.912
6	8.035	1.821	4.718	6	1.964	-3.096	-5.97
6	7.308	1.482	6.056	6	-0.942	-3.415	-5.682
6	9.449	1.162	4.704	6	-0.235	-2.358	-4.937
6	8.234	3.369	4.665	6	1.236	-2.33	-4.952
6	5.786	-2.192	2.353	6	2.006	-4.634	-8.07
6	3.277	-2.873	2.135	6	1.06	-5.396	-9.052
6	1.931	-2.923	2.738	6	2.75	-3.538	-8.896
6	1.787	-2.674	4.181	6	3.036	-5.653	-7.495
6	4.427	-2.46	2.962	6	-2.347	-3.798	-5.459
6	4.223	-2.157	4.386	8	-0.858	-1.312	-4.354
6	2.861	-1.986	4.916	6	2.013	-1.521	-3.938
6	0.679	-3.04	1.895	6	3.566	-4.066	0.042
8	3.415	-2.898	0.788	6	3.594	-3.683	-1.41
6	2.515	-0.875	5.909	6	2.404	-3.294	-2.168
6	3.783	-0.25	6.569	7	2.862	-2.393	-3.153
6	1.763	0.257	5.143	7	4.211	-2.228	-3.028
6	1.609	-1.438	7.046	7	4.679	-2.98	-1.987
6	0.239	-0.527	1.334	7	-4.832	-0.952	-3.954
6	-0.416	0.736	1.713	7	-3.293	-2.972	-4.819
6	-1.407	0.75	2.798	6	-5.112	2.007	-1.553

6	-0.146	-1.776	2.017	6	-4.402	3.189	-1.026
6	-1.262	-1.759	2.976	6	-3.327	3.759	-1.857
6	-1.825	-0.491	3.474	6	-4.582	1.233	-2.688
6	-0.109	2.016	0.971	6	-3.348	1.696	-3.34
8	1.161	-0.499	0.34	6	-2.827	3.037	-3.033
6	-2.796	-0.428	4.659	6	-4.821	3.804	0.313
6	-2.199	0.481	5.778	6	-3.852	4.933	0.788
6	-4.157	0.16	4.176	6	-6.25	4.411	0.174
6	-3.074	-1.829	5.29	6	-4.82	2.7	1.415
6	2.411	2.549	0.593	6	-5.37	0.081	-3.157
6	3.689	3.044	1.138	8	-2.575	0.901	-4.108
6	3.674	3.848	2.369	6	-6.728	-4.753	-4.865
6	1.209	2.585	1.446	6	-6.979	-2.31	-4.207
6	1.259	3.248	2.758	6	-7.58	-3.614	-4.507
6	2.49	3.893	3.247	6	-5.52	-2.15	-4.262
6	5.033	2.642	0.568	6	-4.674	-3.267	-4.711
1	2.395	0.655	4.346	6	-5.274	-4.583	-4.967
1	1.505	1.066	5.828	6	-1.764	3.661	-3.905
1	0.845	-0.127	4.7	6	2.761	2.617	-1.83
1	2.11	-2.271	7.544	6	1.626	2.736	-2.8
1	0.657	-1.789	6.645	6	0.427	3.55	-2.628
1	1.404	-0.66	7.784	7	-0.471	3.081	-3.609
1	0.92	-3.217	0.848	7	0.142	2.132	-4.377
1	0.1	-3.896	2.249	7	1.397	1.876	-3.897
1	-1.826	1.669	3.09	12	-2.82	-1.054	-4.3
1	-1.589	-2.673	3.375	8	-2.725	-1.859	-2.432
1	-2.037	1.495	5.41	6	-2.355	-0.844	-1.553
1	-1.246	0.075	6.12	8	-1.096	-0.26	-1.67
1	-2.883	0.529	6.628	8	-3.286	-0.664	-6.243
1	-4.032	1.193	3.852	6	-2.09	-0.467	-6.934
1	-4.886	0.141	4.988	8	-1.35	0.692	-6.708
1	-4.544	-0.428	3.341	6	-1.879	-1.202	-8.229
1	-2.143	-2.279	5.64	6	-3.093	-0.731	-0.249
1	-3.542	-2.49	4.558	1	7.353	-0.822	4.142
1	-3.749	-1.729	6.143	1	6.865	3.186	2.504
1	-0.081	1.815	-0.1	1	7.207	0.403	6.179
1	-0.9	2.748	1.149	1	6.313	1.932	6.063
1	4.561	4.322	2.674	1	7.875	1.874	6.903
1	0.384	3.269	3.339	1	9.375	0.082	4.842
1	4.675	3.994	4.983	1	10.063	1.569	5.51
1	3.487	2.813	5.561	1	9.944	1.36	3.751
1	3.752	4.321	6.457	1	7.269	3.878	4.693
1	3.905	6.191	3.939	1	8.764	3.653	3.755
1	2.97	6.585	5.389	1	8.822	3.702	5.523
1	2.175	6.559	3.803	1	6.543	-2.73	2.927

1	0.971	3.451	5.599	1	0.837	-2.767	4.62
1	0.45	4.997	4.89	1	5.055	-1.934	4.987
1	1.375	4.977	6.399	1	4.421	0.204	5.808
1	5.654	3.534	0.469	1	4.35	-1.016	7.101
1	4.932	2.207	-0.423	1	3.494	0.525	7.281
1	5.829	-2.552	1.325	1	0.139	3.999	-1.728
1	-0.687	-4.976	-7.18	1	-1.967	-2.48	-2.45
1	3.011	-3.015	-6.017	1	-3.733	0.208	-6.232
1	1.633	-5.794	-9.892	1	-2.352	-0.651	-9.042
1	0.296	-4.721	-9.442	1	-0.811	-1.295	-8.428
1	0.576	-6.232	-8.545	1	-2.32	-2.197	-8.166
1	3.252	-3.989	-9.754	1	-4.159	-0.893	-0.412
1	3.501	-3.036	-8.285	1	-2.72	-1.481	0.447
1	2.036	-2.795	-9.257	1	-2.944	0.263	0.172
1	3.767	-5.146	-6.863	1	1.438	0.341	-0.034
1	3.567	-6.152	-8.308	1	4.492	-1.289	0.435
1	2.521	-6.408	-6.897	1	-6.259	5.168	-0.612
1	-2.681	-4.694	-5.898	1	-5.546	1.919	1.185
1	1.336	-0.99	-3.267	1	-5.077	3.133	2.383
1	2.625	-0.785	-4.463	1	-3.829	2.249	1.484
1	2.737	-4.75	0.227	1	-6.341	-0.036	-2.77
1	4.503	-4.559	0.305	1	-7.16	-5.691	-5.056
1	1.438	-3.268	-1.763	1	-7.601	-1.493	-3.99
1	-5.986	1.672	-1.075	1	-4.674	-5.413	-5.195
1	-2.903	4.689	-1.617	1	-8.623	-3.734	-4.462
1	-4.152	5.296	1.774	1	-1.728	4.739	-3.738
1	-3.877	5.775	0.094	1	-2.01	3.489	-4.955
1	-2.831	4.553	0.856	1	3.167	3.611	-1.636
1	-6.554	4.877	1.114	1	3.538	1.99	-2.268
1	-6.974	3.635	-0.078				

SI 14 Microscopy image and size distribution plots for L and L with Mg^{2+}

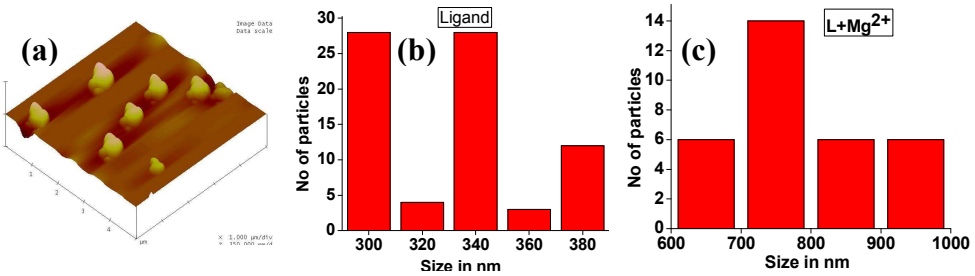


Figure SI34 AFM and SEM images and size distribution plots (a) 3D AFM image of {**L**+Mg^{2+}}. Size distribution plots of SEM images (b) for **L** (c) for {**L**+Mg^{2+}}.