Electronic Supplementary Information

Amino-ether macrocycle that forms Cu^{II} templated threaded heteroleptic complexes: A detailed selectivity, structural and theoretical investigations

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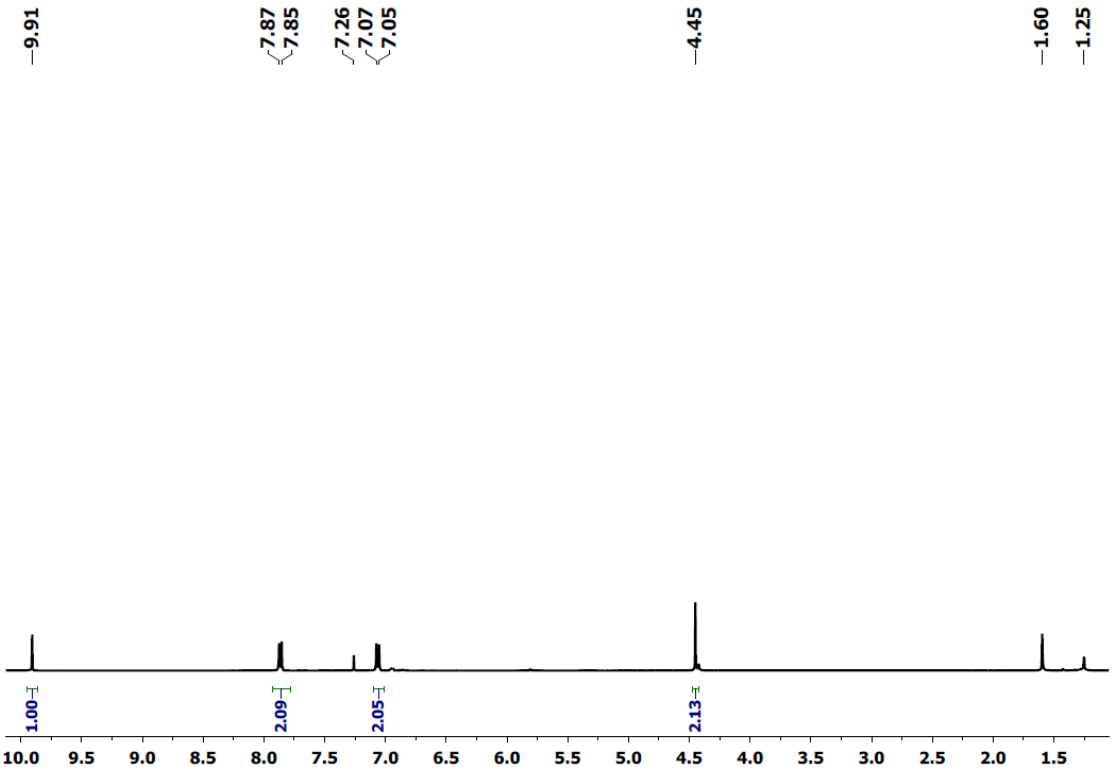


Figure 1S. ^{1}H-NMR Spectrum of Compound **I** in $CDCl_3$ (400 MHz).

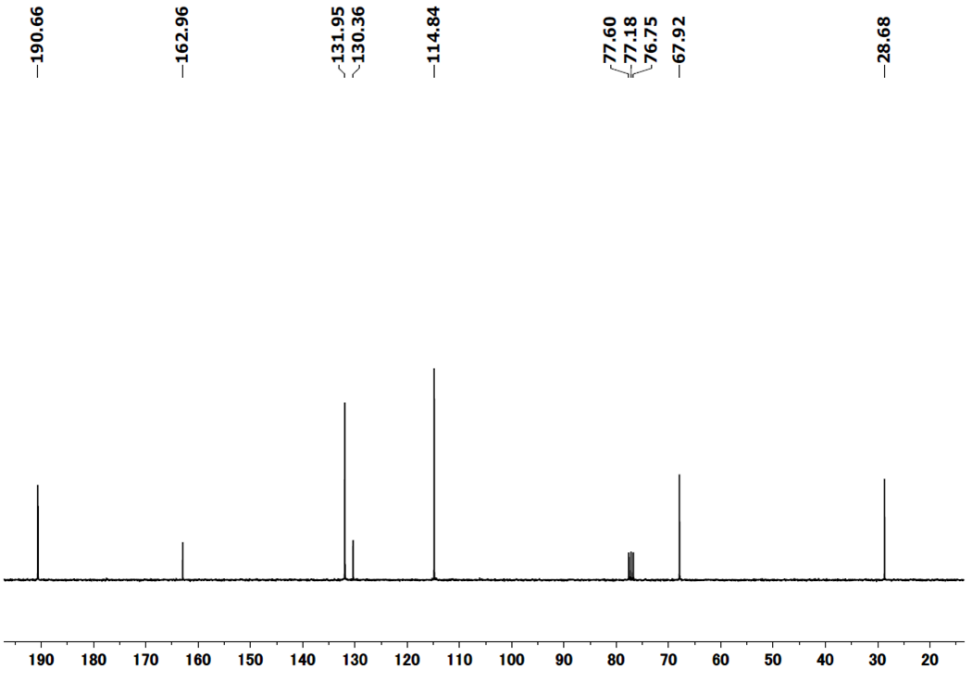


Figure 2S. ^{13}C-NMR Spectrum of Compound **I** in $CDCl_3$ (75 MHz).

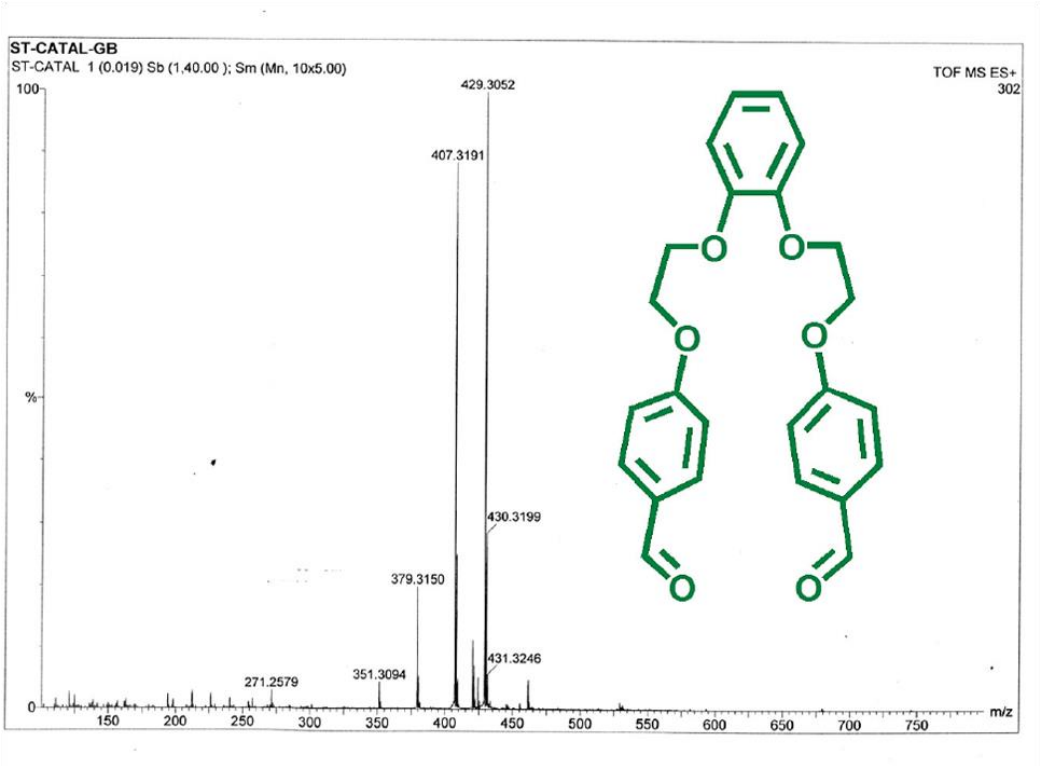


Figure 3S. ESI-MS Spectrum of Compound **II**.

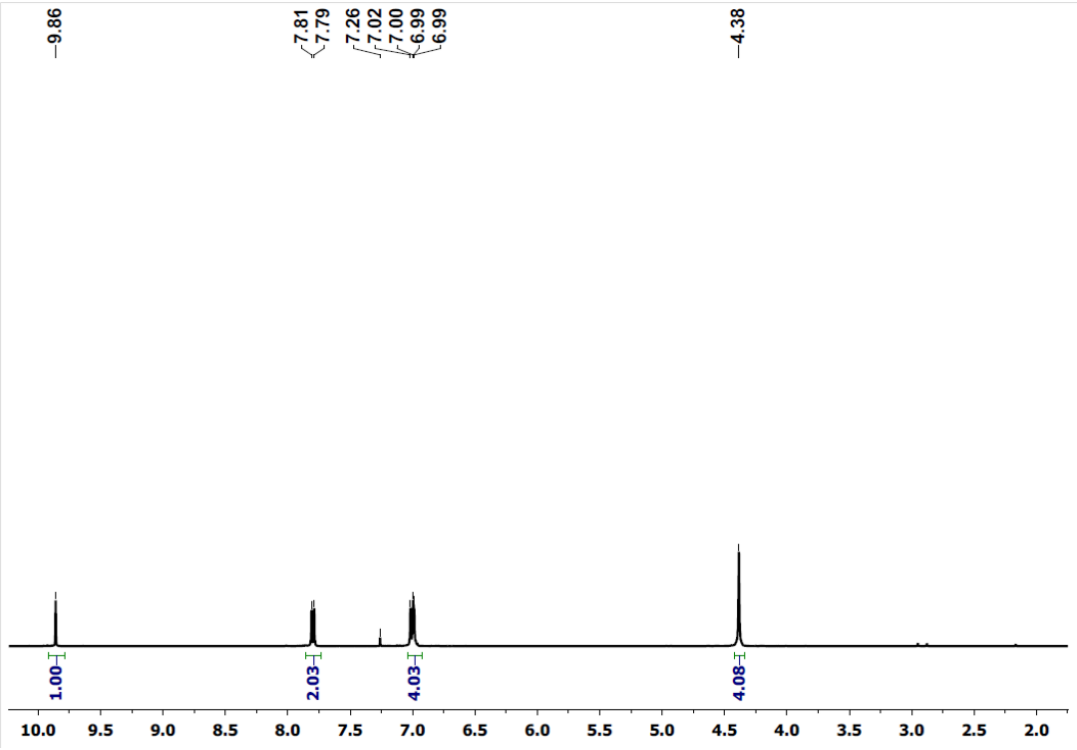


Figure 4S. ^{1}H-NMR Spectrum of Compound **II** in $CDCl_3$ (400 MHz).

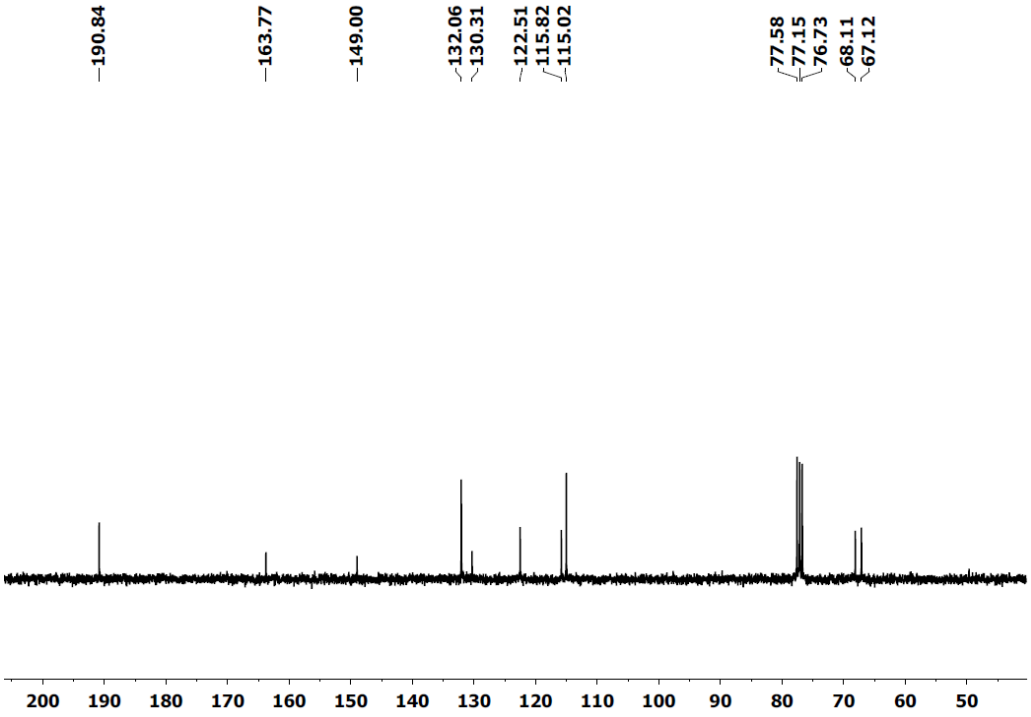


Figure 5S. ^{13}C-NMR Spectrum of Compound **II** in $CDCl_3$ (75 MHz).

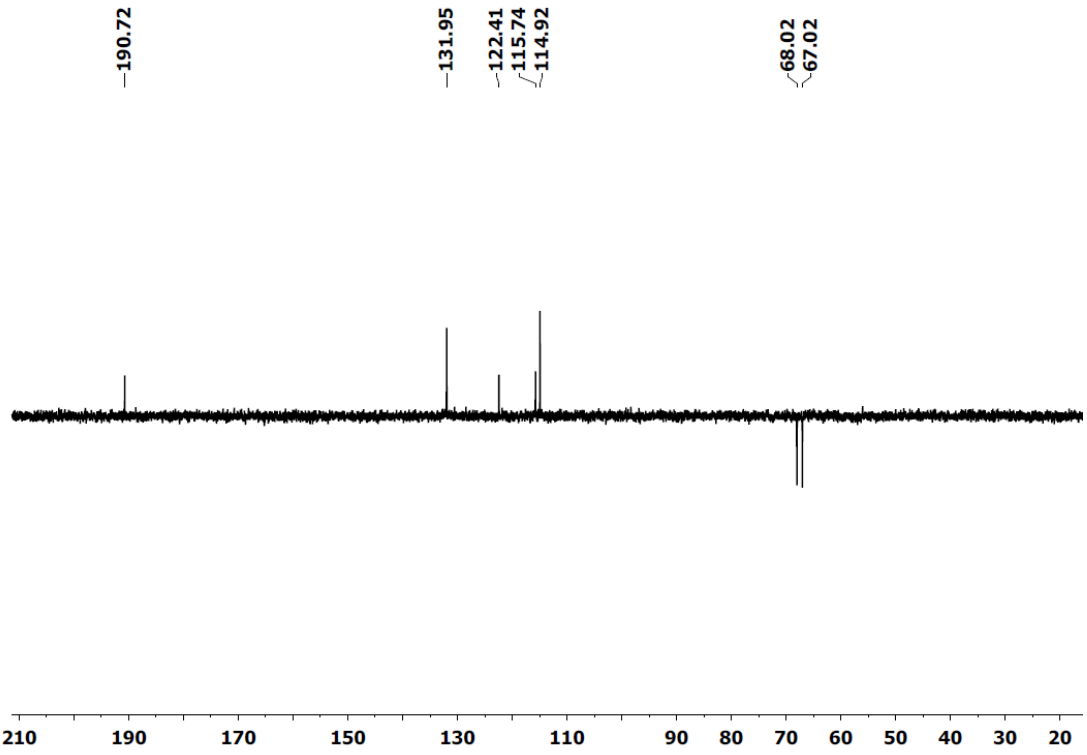


Figure 6S. DEPT-135 NMR Spectrum of Compound **II** in $CDCl_3$ (300 MHz).

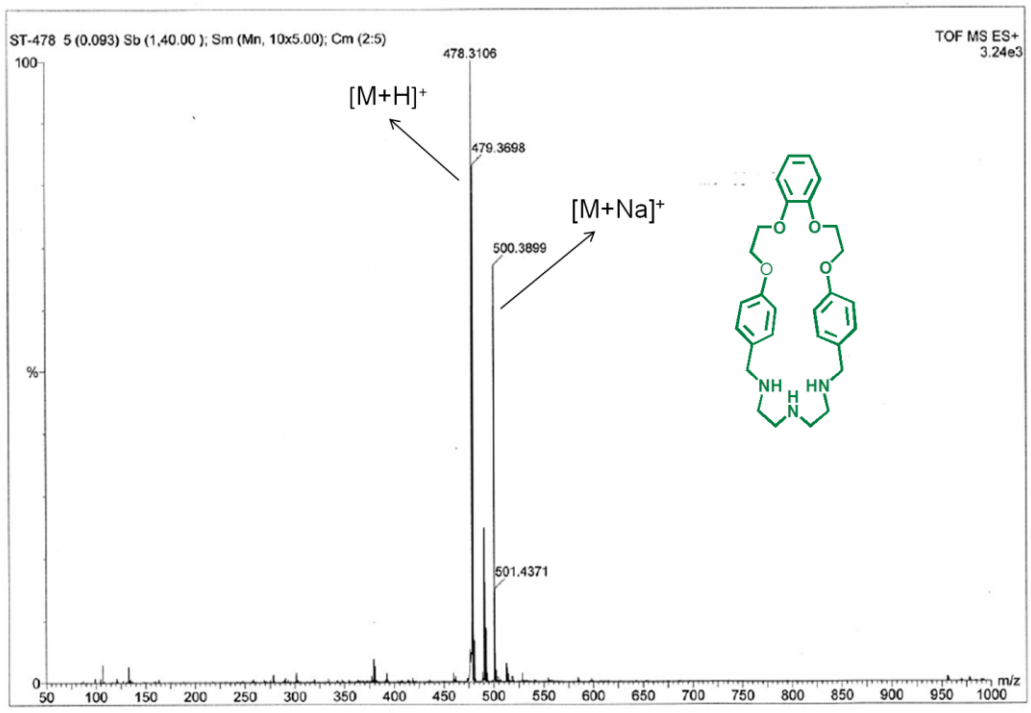


Figure 7S. ESI-MS of compound **MC**.

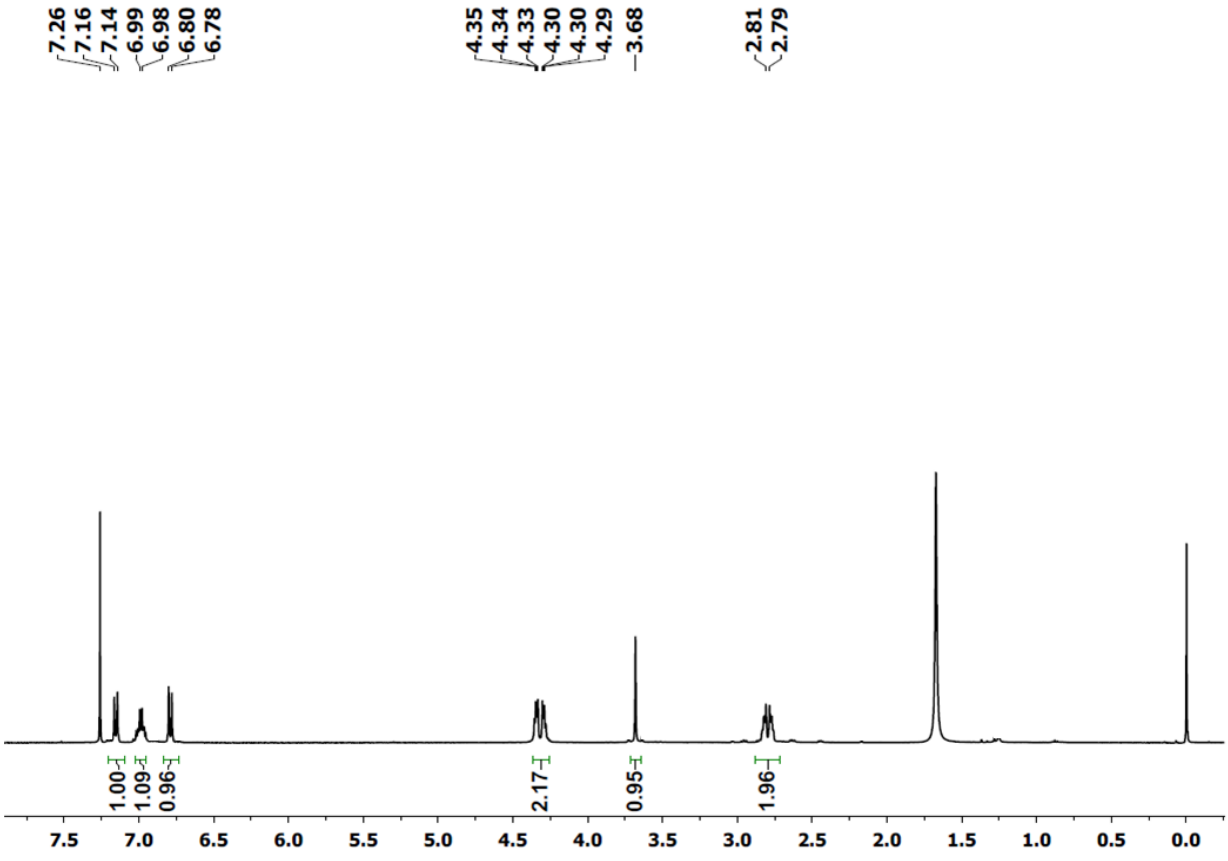


Figure 8S. ^{1}H-NMR Spectrum of Compound **MC** in $CDCl_3$ (400 MHz).

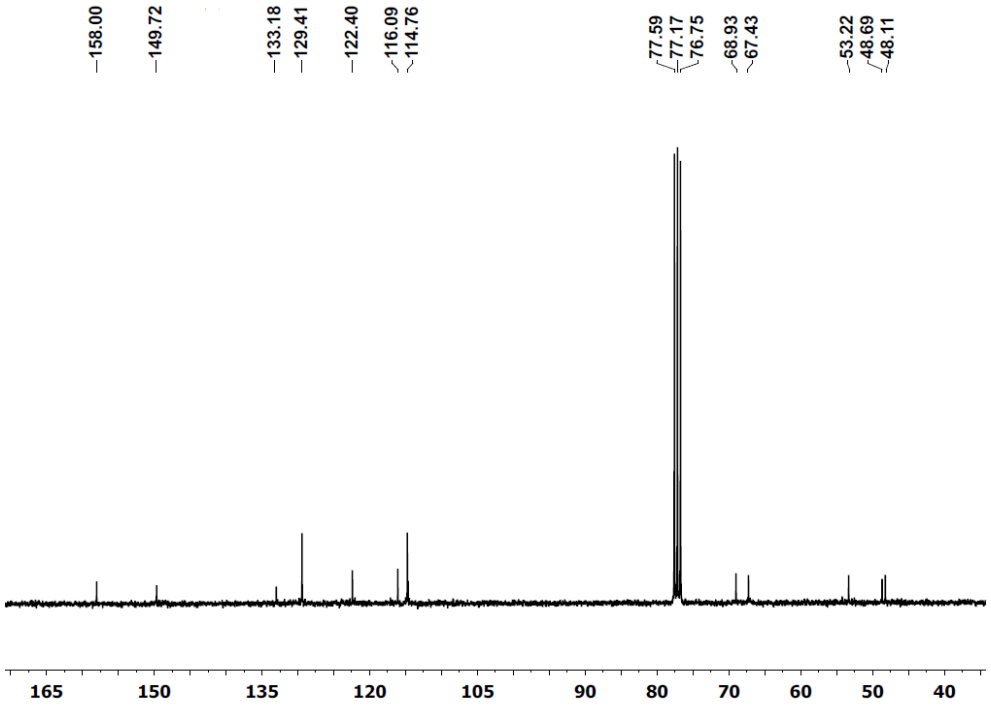


Figure 9S. ^{13}C-NMR Spectrum of Compound **MC** in $CDCl_3$ (75 MHz).

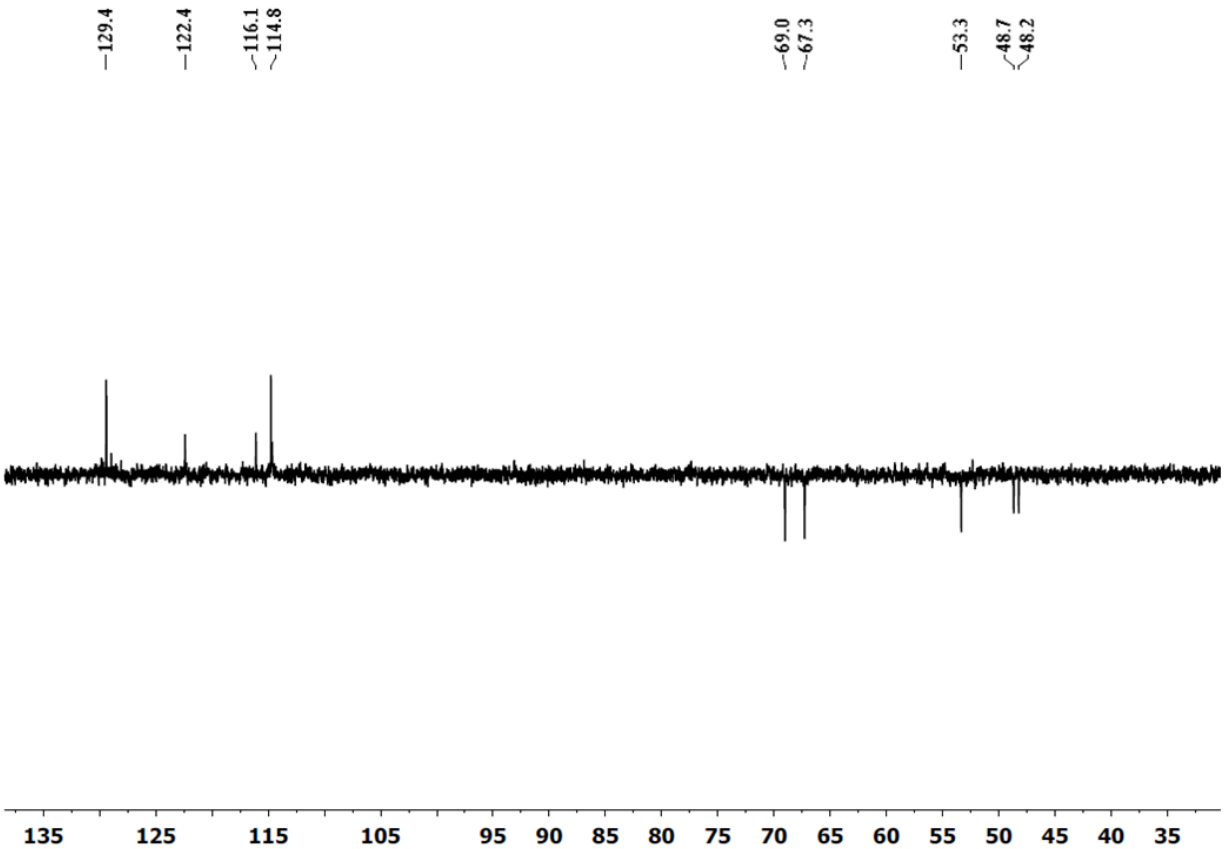
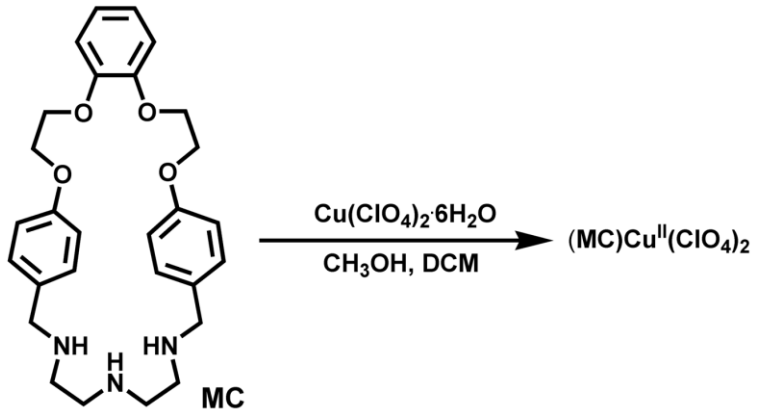
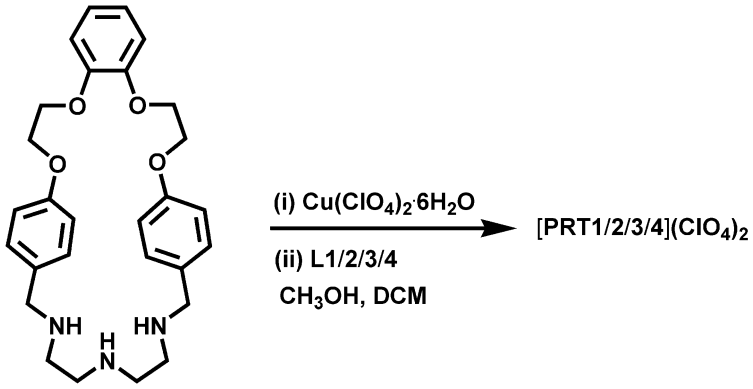


Figure 10S. DEPT-135 NMR Spectrum of Compound **MC** in $CDCl_3$ (300 MHz).



Scheme 1S. Synthetic route for the preparation of the **MC-Cu^{II}**·2ClO$_4$ complex.



Scheme 2S. Synthetic route for the preparation of the complexes **PRT1-PRT4**.

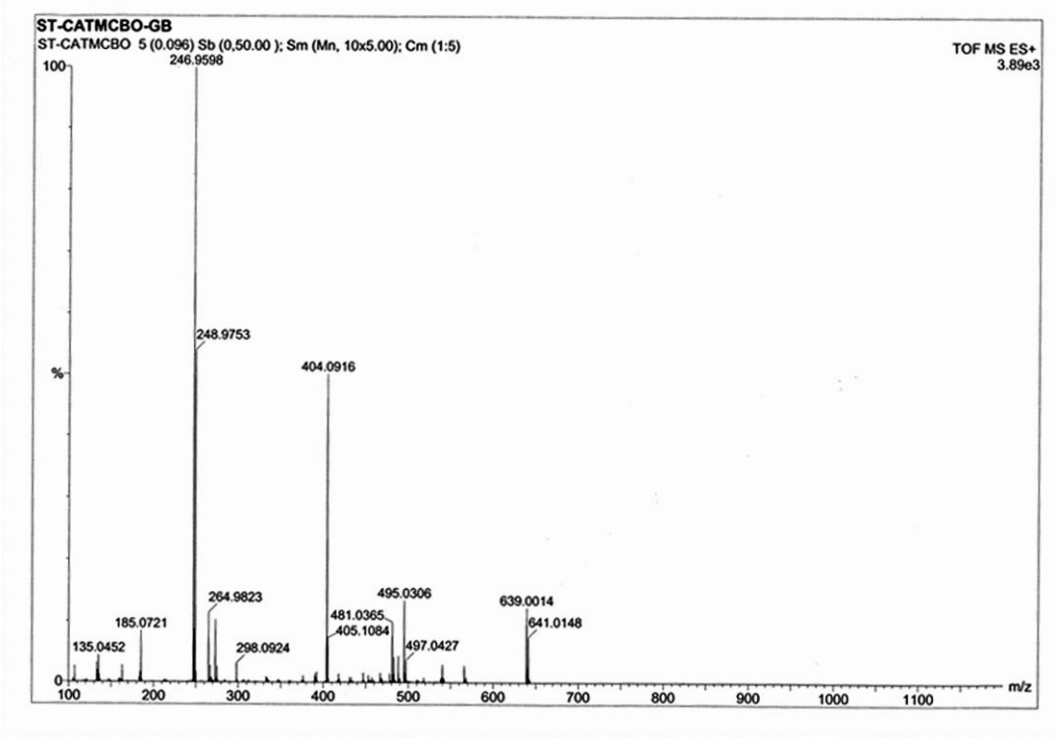


Figure 11S. ESI-MS of compound (MC)Cu^{II}(ClO$_4$)$_2$.

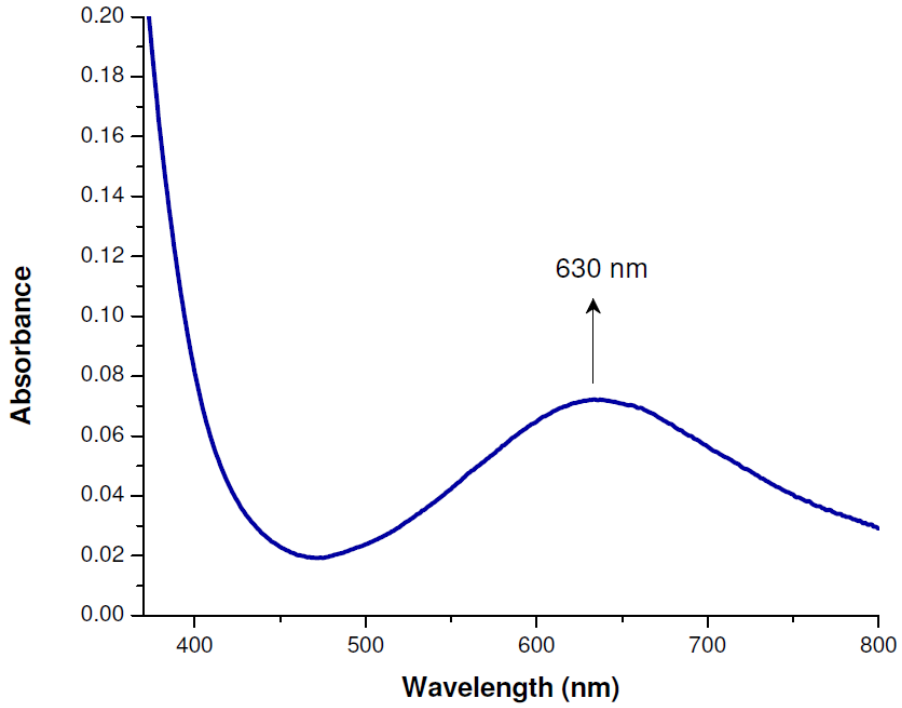


Figure 12S. UV/Vis spectrum of the (**MC**)$Cu^{II}(ClO_4)_2$ complex in methanol.

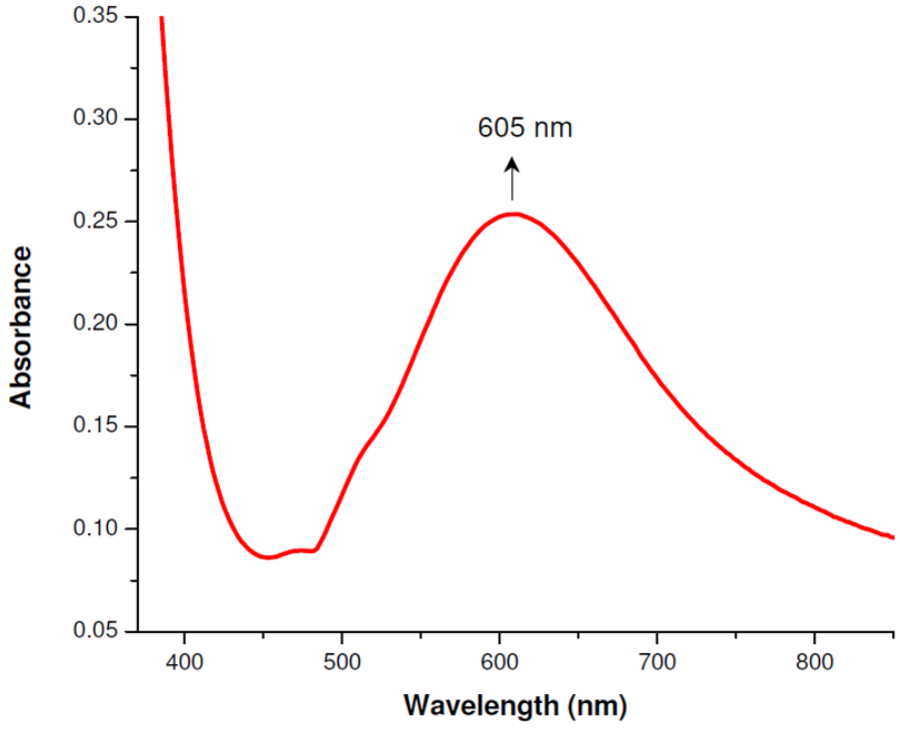
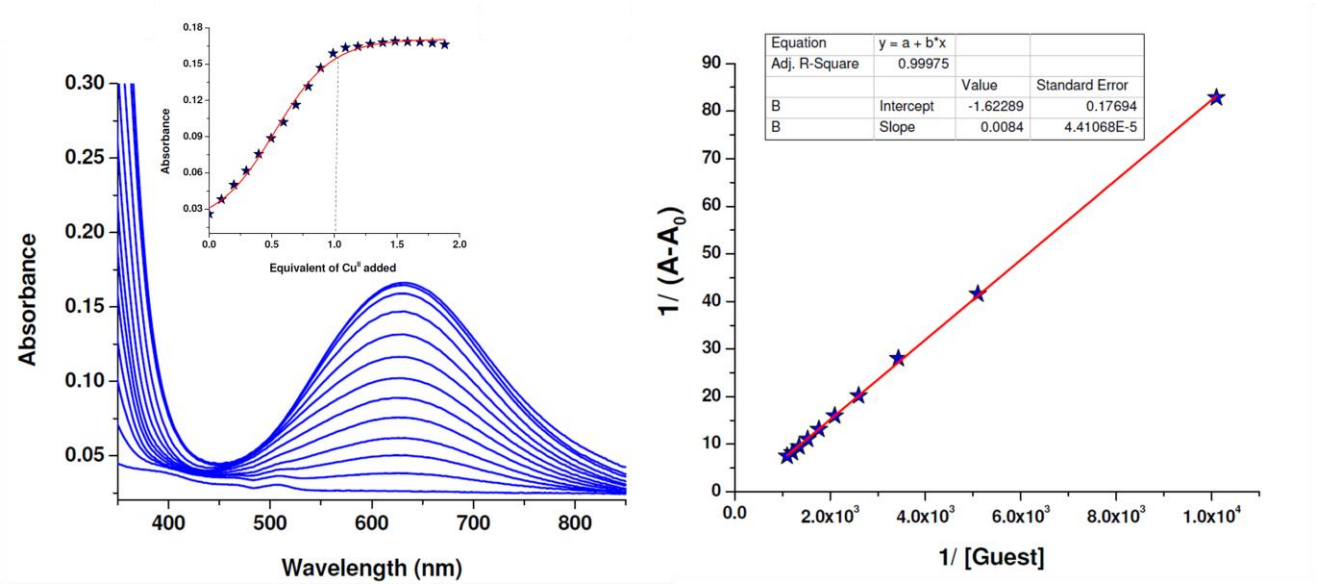


Figure 13S. UV/Vis spectrum of the (**MC**)$Cu^{II}(ClO_4)_2$ complex in acetonitrile.



(a) **(b)**

Figure 14S. (a) UV/Vis Titration profile of **MC** (1×10^{-3} M) with the aliquots of $Cu(ClO_4)_2.6H_2O$ (1×10^{-2} M) in methanol (selected UV/Vis spectra are shown for clarity whereas equivalent plot shows more point) and equivalent plot of the (**MC**)$Cu^{II}(ClO_4)_2$ complex, (b) Benesi-Hildebrand Plot of the (**MC**)$Cu^{II}(ClO_4)_2$ complex.

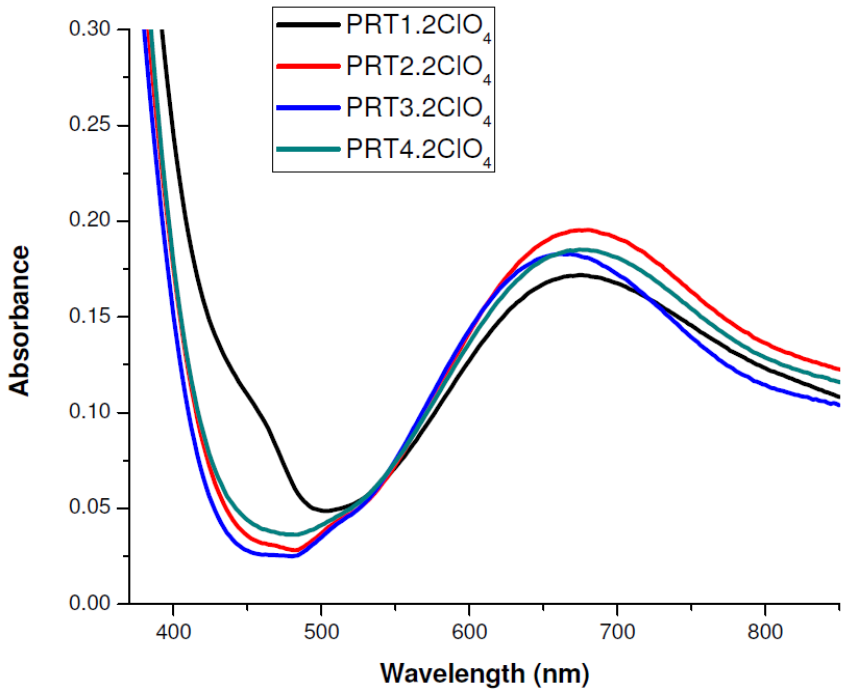


Figure 15S. UV/Vis Spectrum of **PRT1**-**PRT4** having ClO_4^- counter anions in acetonitrile.

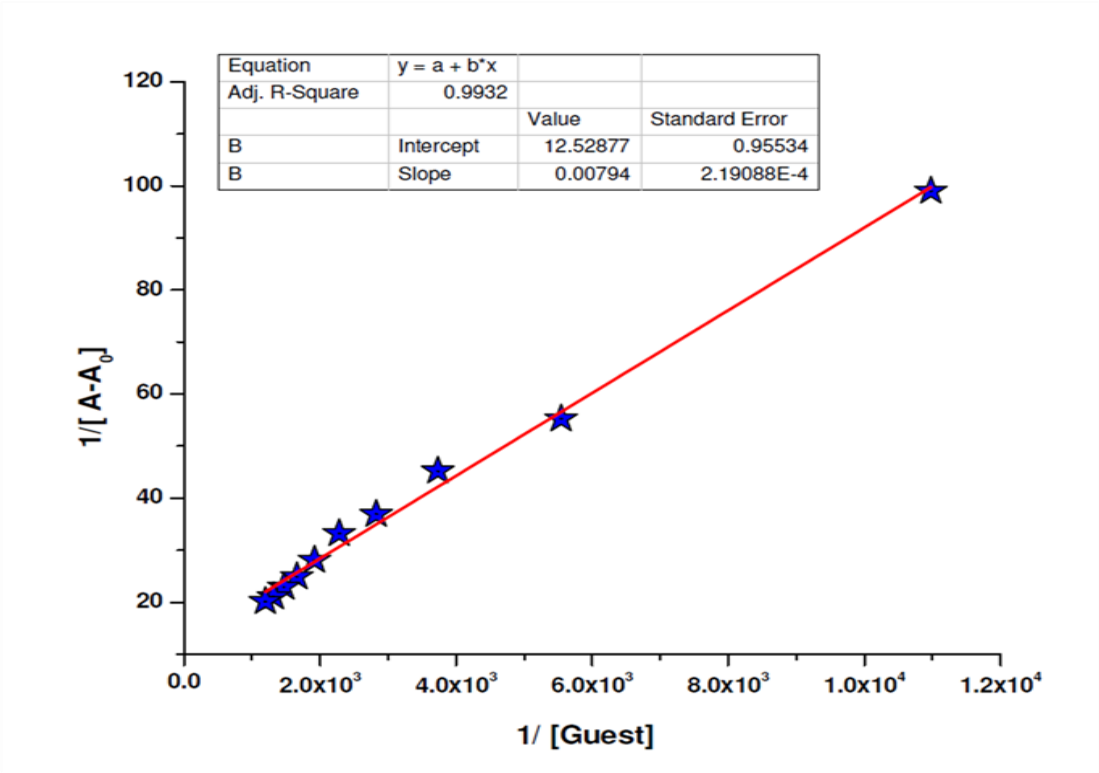


Figure 16S. Benesi-Hildebrand plot of the **PRT1**·2ClO_4^- complex.

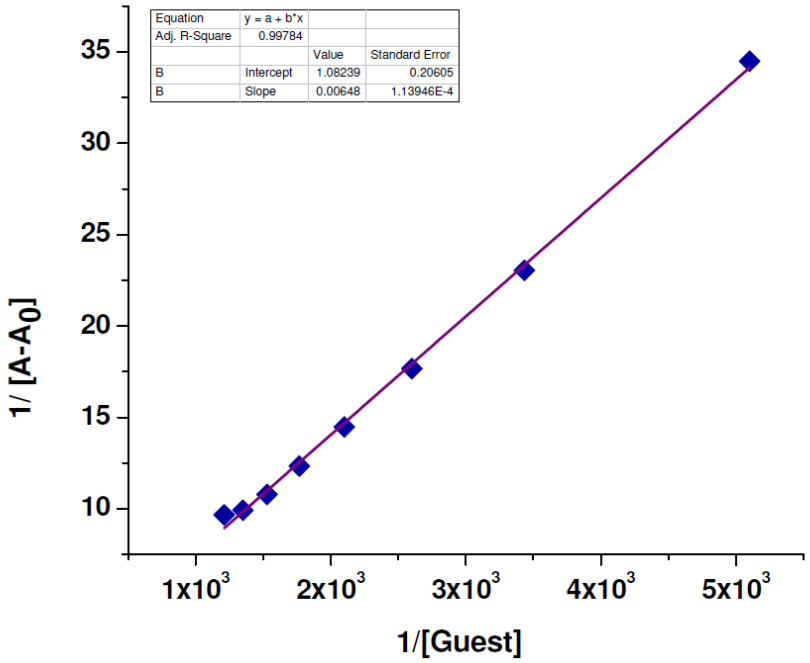


Figure 17S. Benesi-Hildebrand plot of the **PRT2**·2ClO_4^- complex.

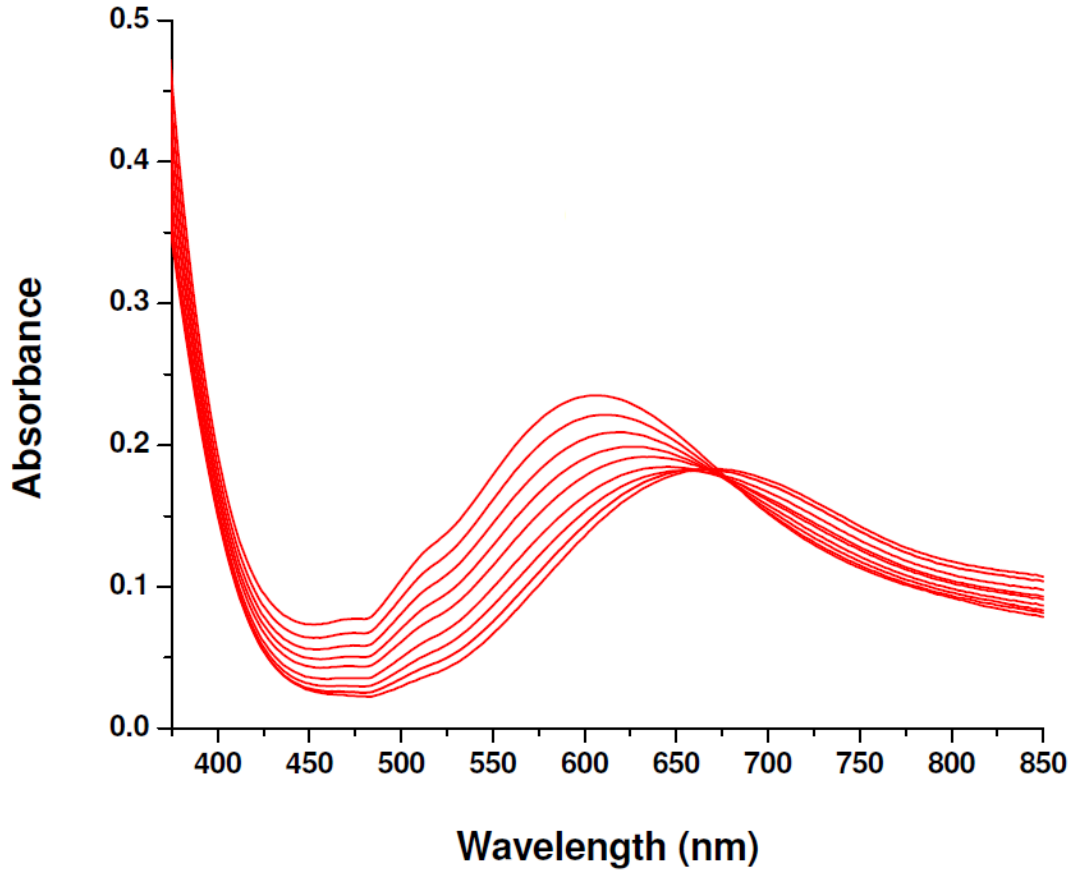


Figure 18S. UV/Vis titration profile of (MC)$Cu^{II}(ClO_4)_2$ complex with **L3** (selected UV/Vis spectra are shown for clarity).

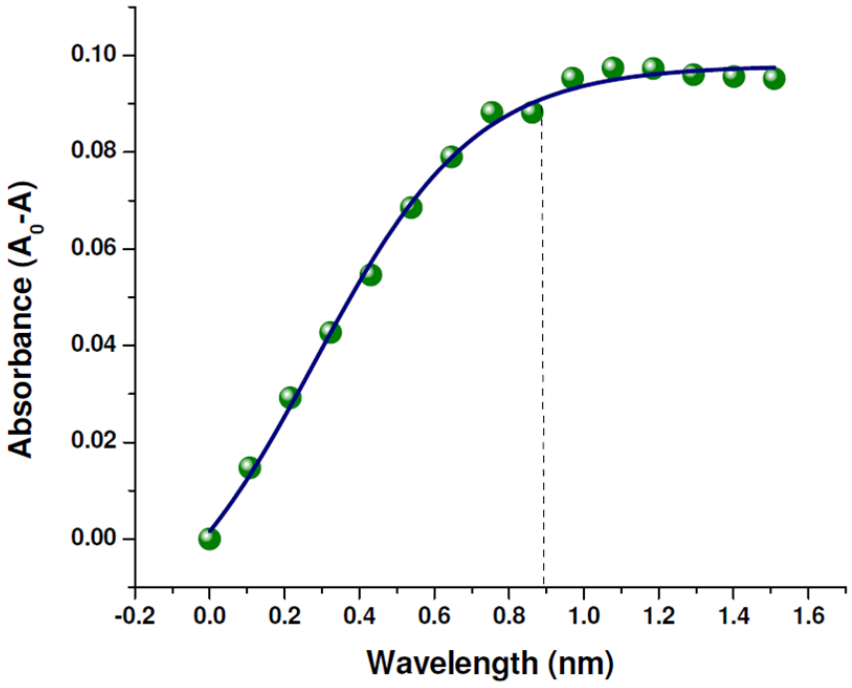


Figure 19S. Equivalent plot of the **PRT3**·$2ClO_4^-$ complex.

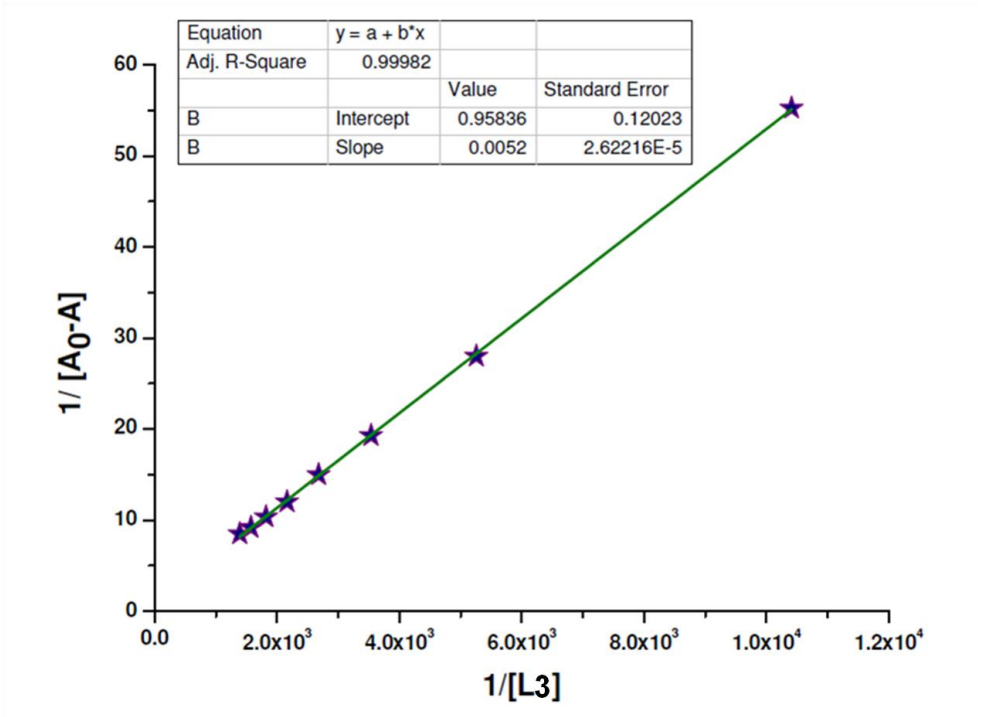


Figure 20S. Benesi-Hildebrand plot of the **PRT3**·$2ClO_4^-$ complex.

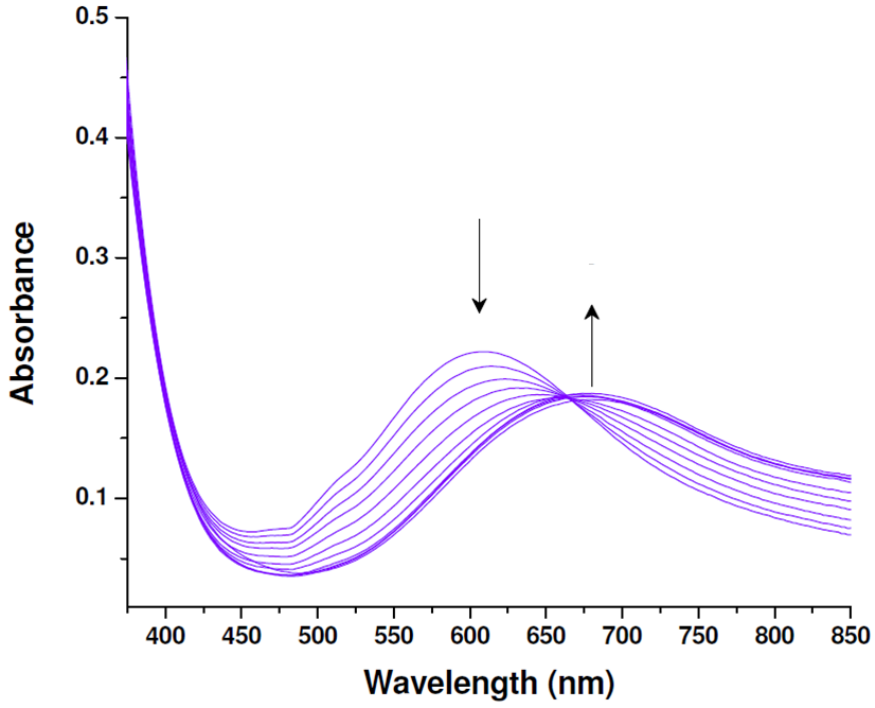


Figure 21S. UV/Vis titration profile of (**MC**)$Cu^{II}(ClO_4)_2$ complex with **L4** (selected UV/Vis spectra are shown for clarity).

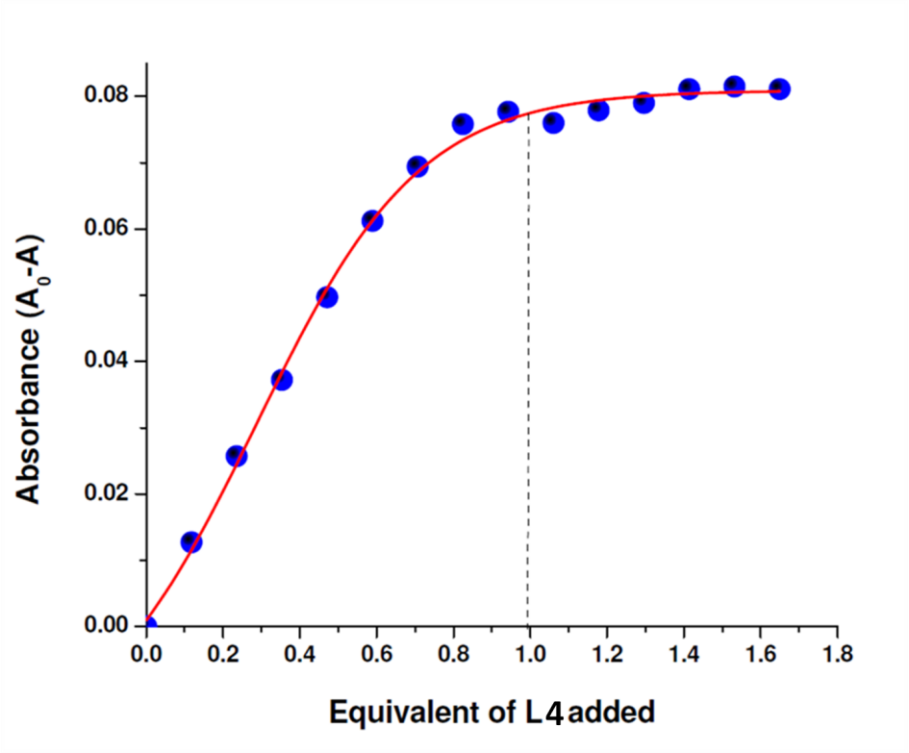


Figure 22S. Equivalent plot of the **PRT4**·2ClO_4^- complex.

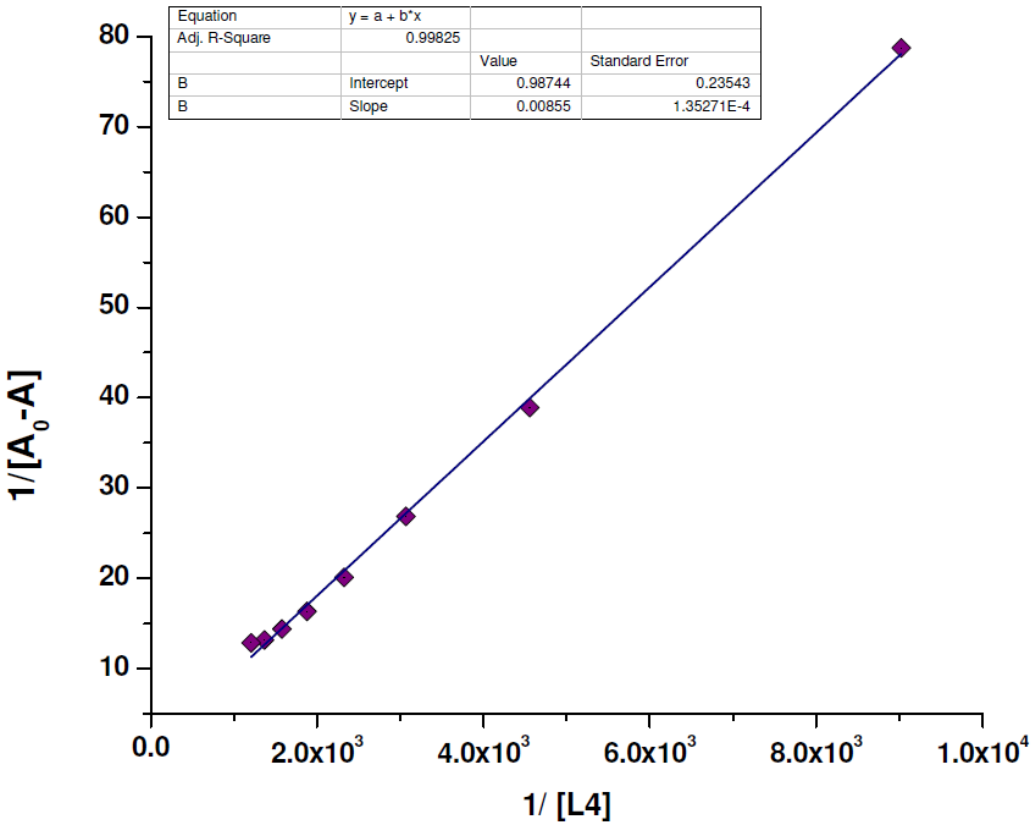


Figure 23S. Benesi-Hildebrand plot of the **PRT4**·2ClO_4^- complex.

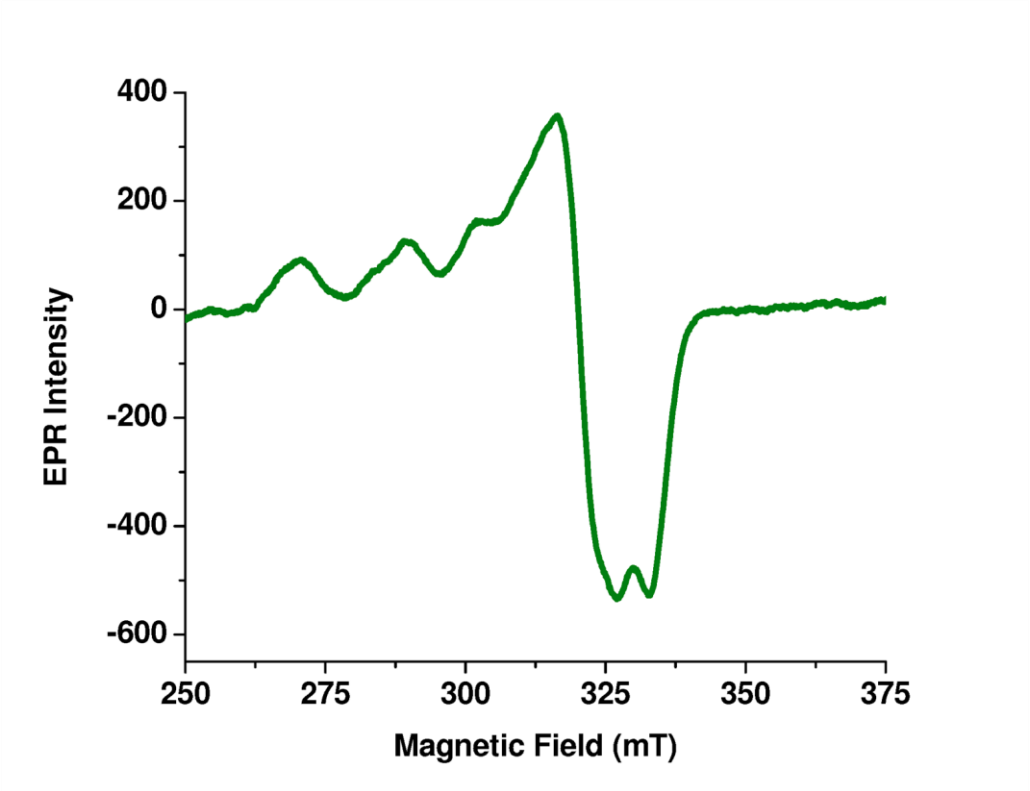


Figure 24S. EPR Spectrum of **PRT3**·2ClO_4^- in acetonitrile at 80 K.

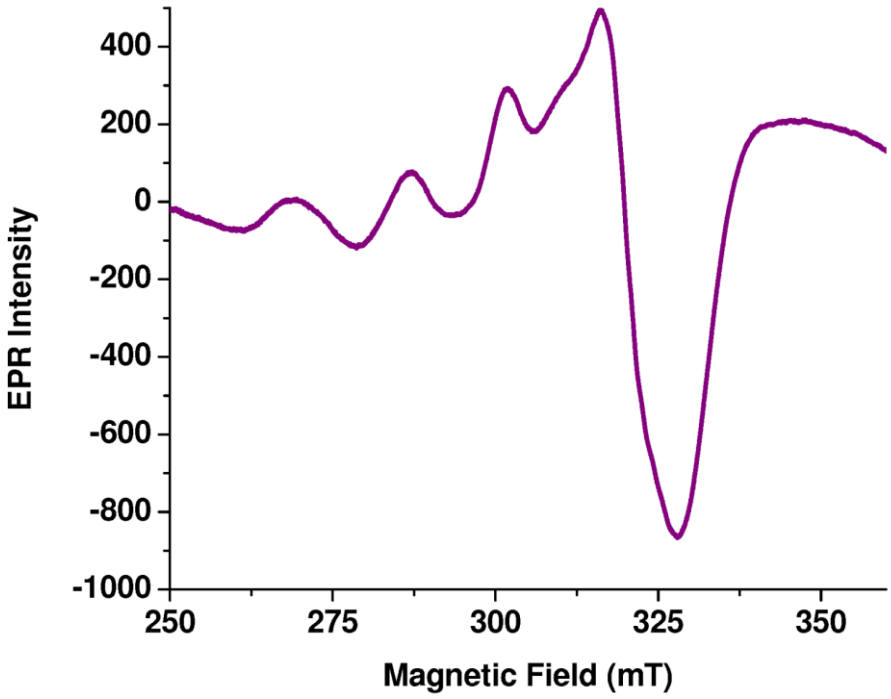


Figure 25S. EPR Spectrum of **PRT4**·2ClO_4^- in acetonitrile at 80 K.

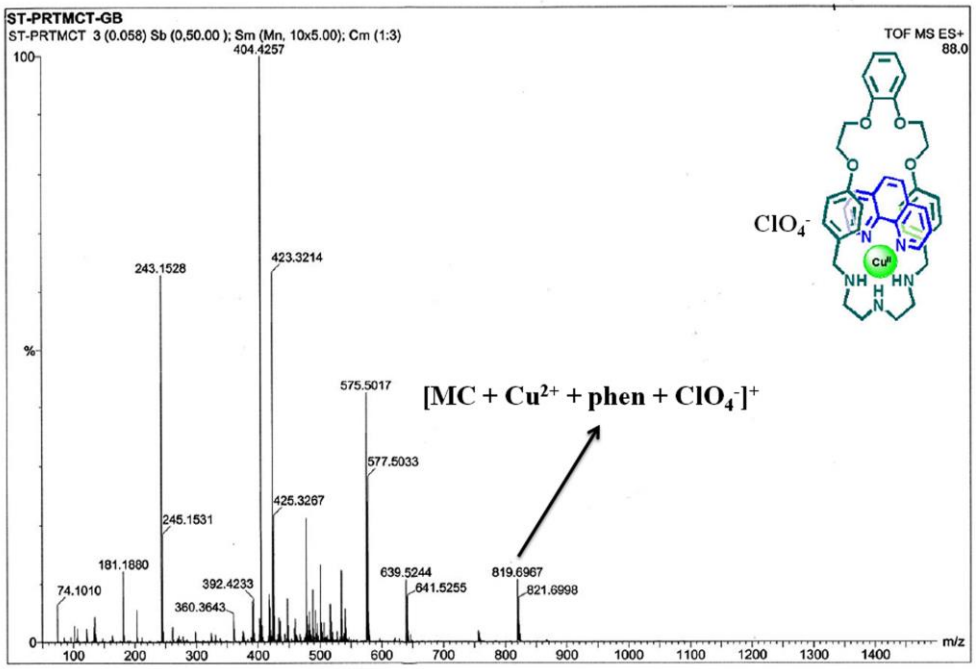


Figure 26S. ESI-MS of compound **PRT1** with ClO_4^- counter anion.

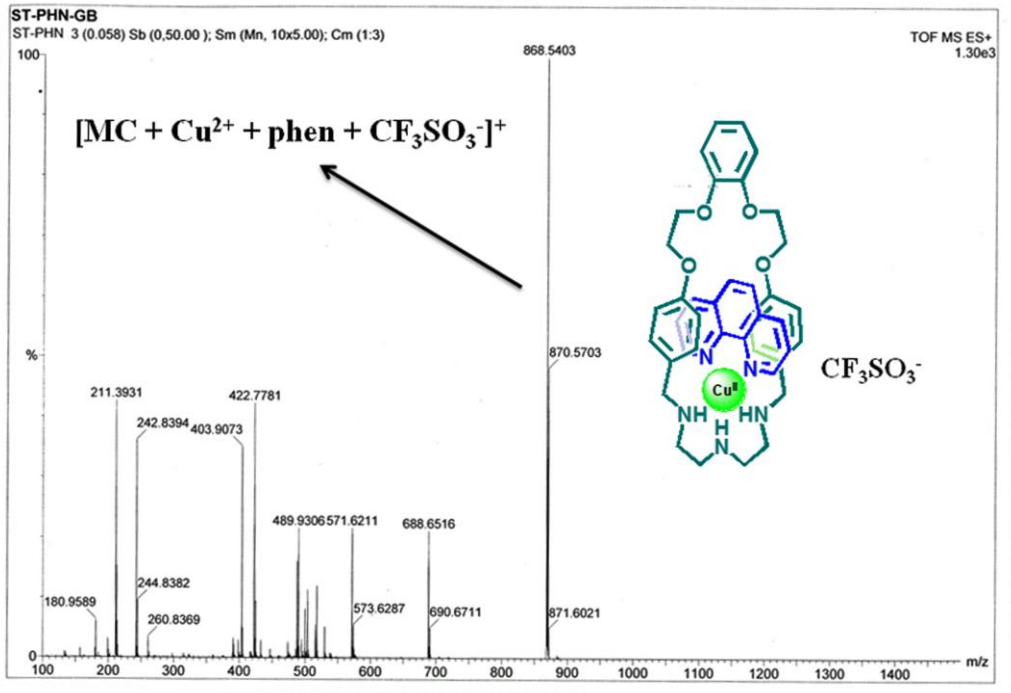


Figure 27S. ESI-MS of compound **PRT1** with OTf $^-$ counter anion.

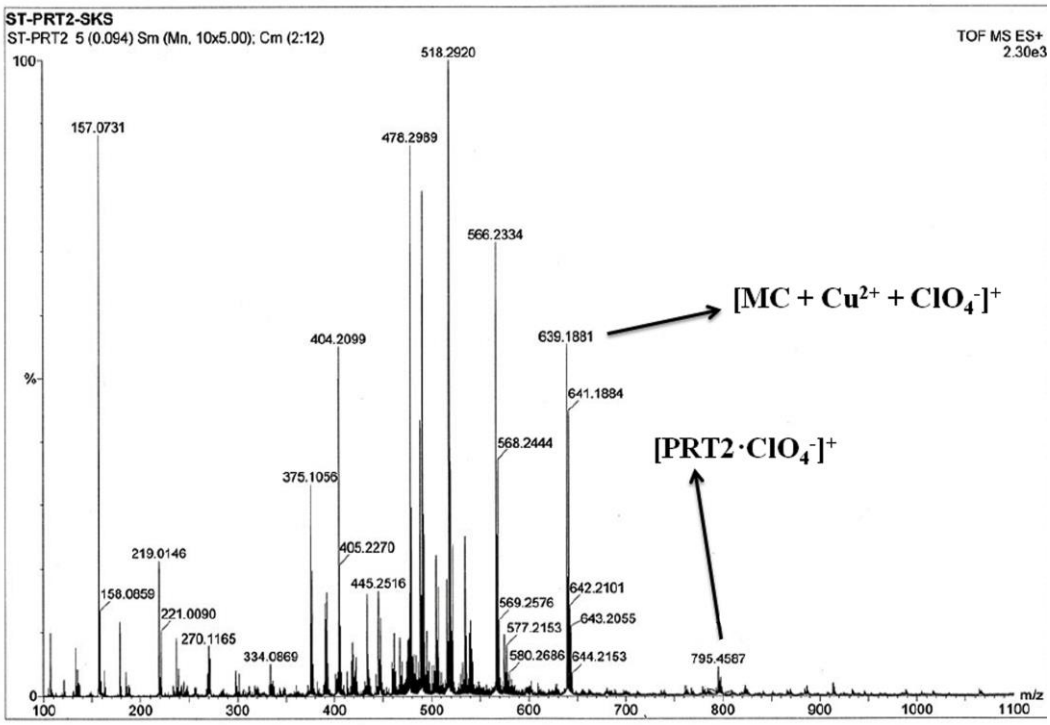


Figure 28S. ESI-MS of compound **PRT2** with ClO_4^- counter anion.

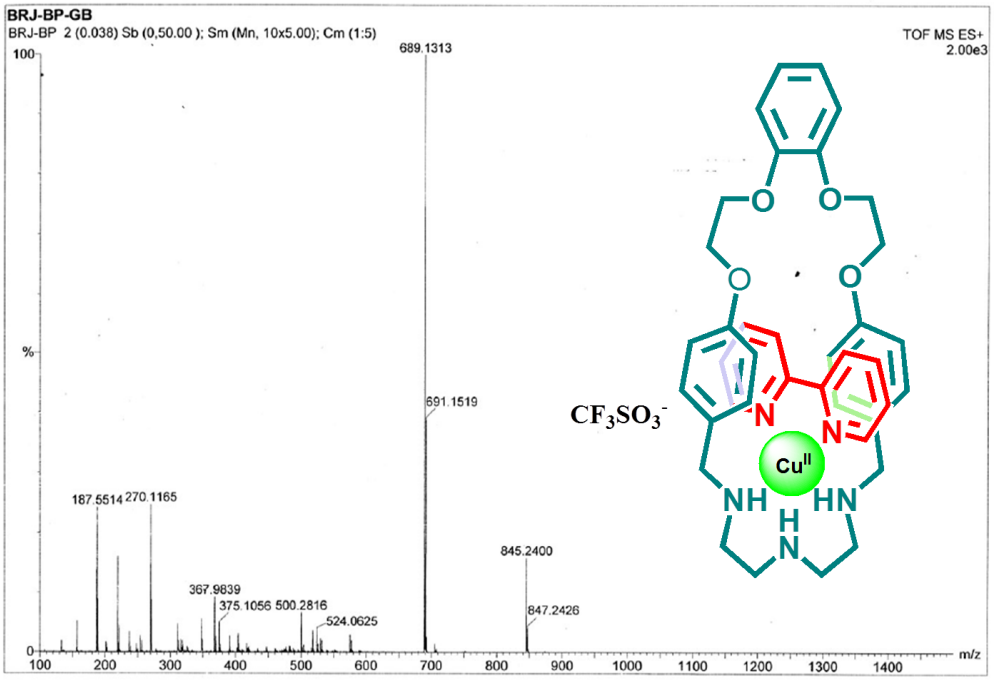


Figure 29S. ESI-MS of compound **PRT2** with OTf $^-$ counter anion.

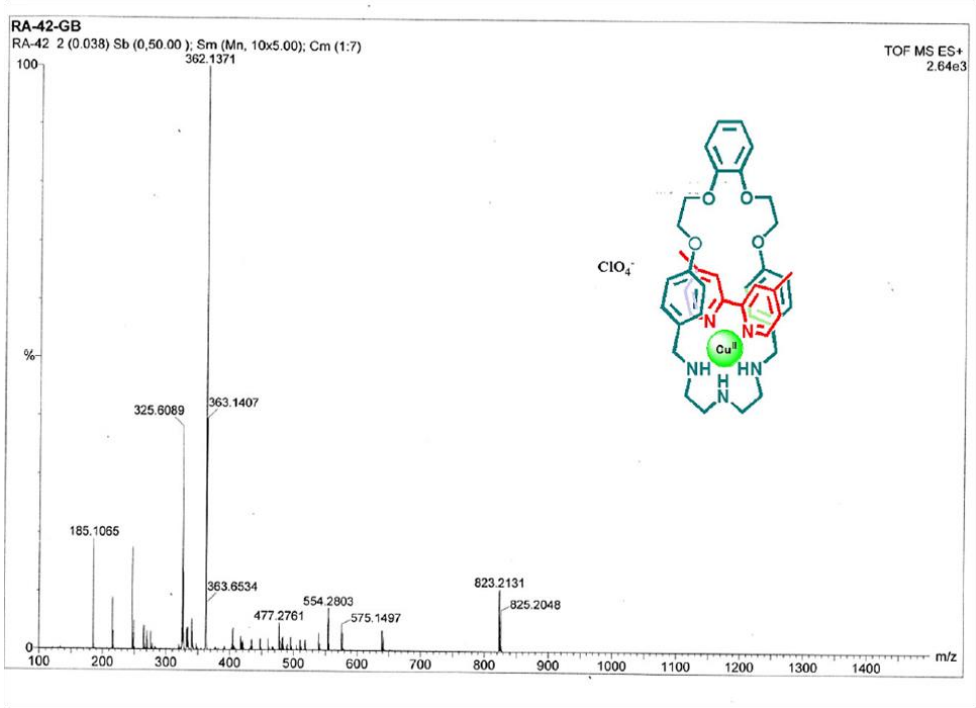


Figure 30S. ESI-MS of compound **PRT3** with ClO_4^- counter anion.

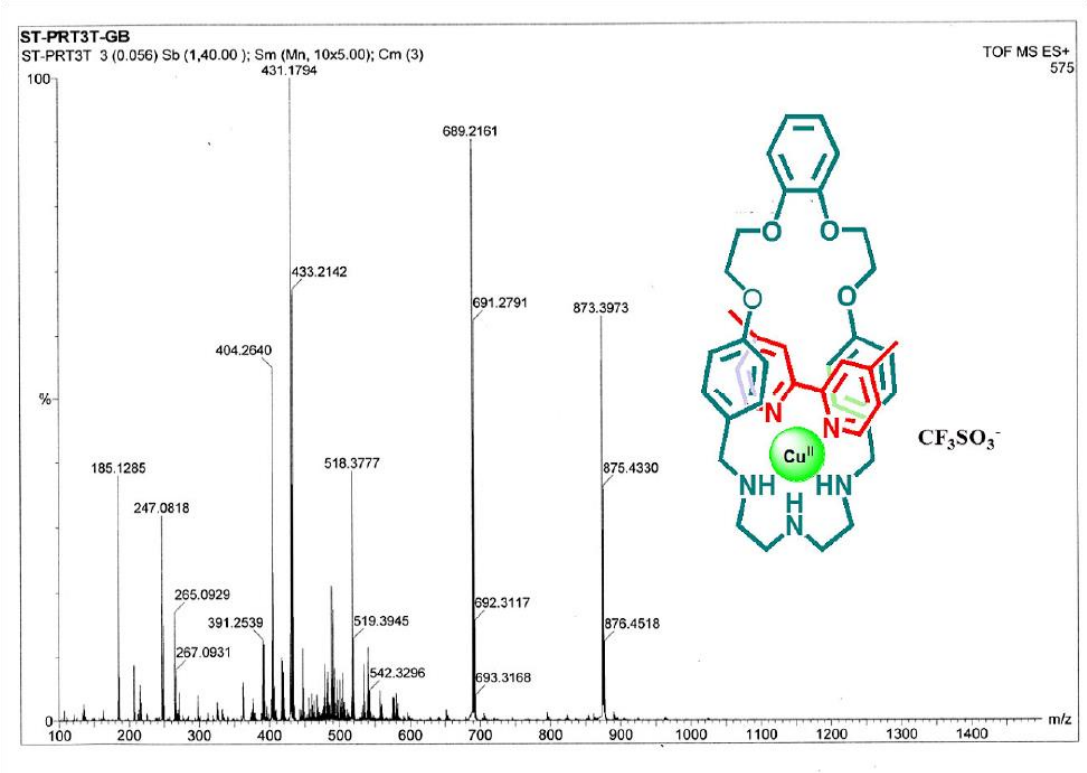


Figure 31S. ESI-MS of compound **PRT3** with OTf $^-$ counter anion.

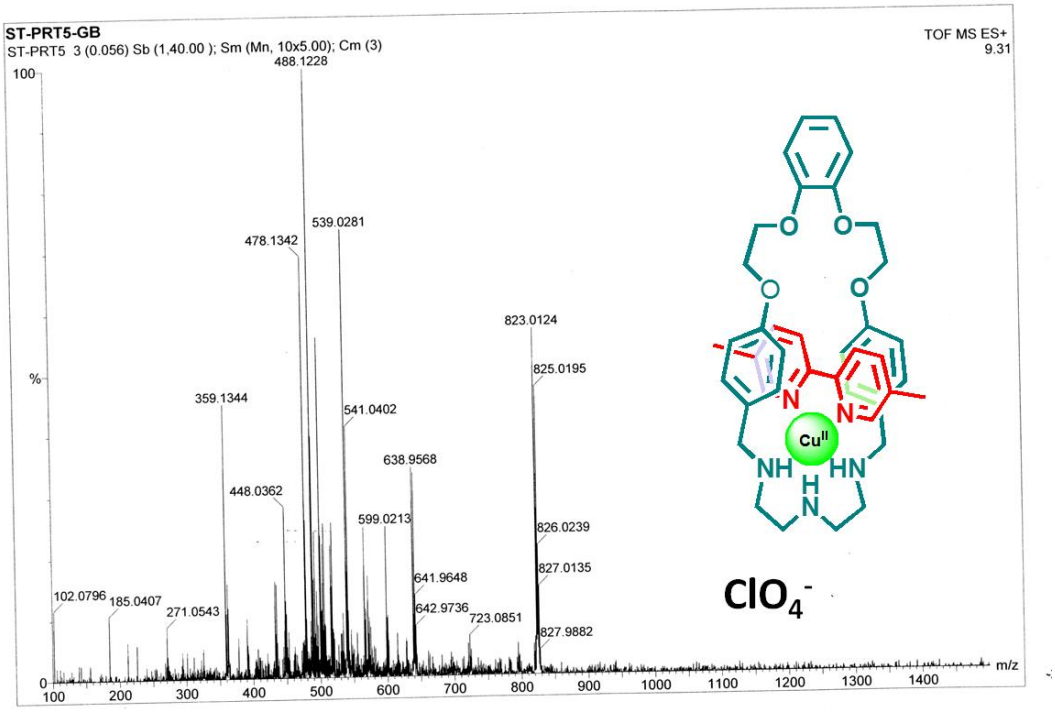


Figure 32S. ESI-MS of compound **PRT4** with ClO_4^- counter anion.

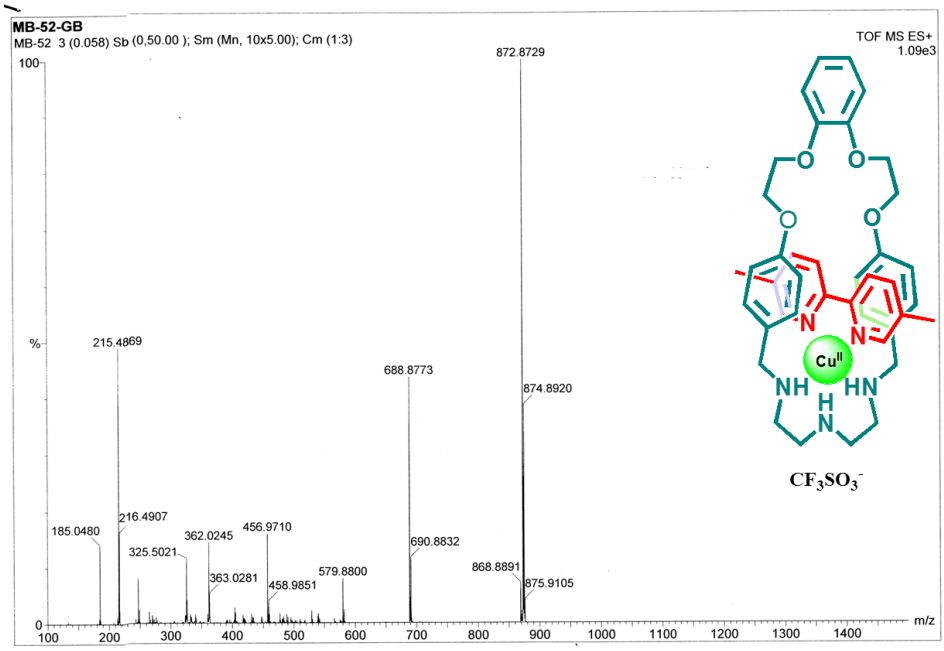


Figure 33S. ESI-MS of compound **PRT4** with OTf^- counter anion.

Table 1S. Selected Bond Distances (Å) and Angles (deg) for **MC-Cu^{II}** and **PRT1**-**PRT4**

MC-Cu^{II}					
Cu1-N1	2.052(10)	Cu1-N2	1.990(12)	Cu1-N3	2.064(10)
Cu1-N4	1.963(13)	Cu1-N5	2.292(14)	N1-C17	1.498(20)
N1-C18	1.520(20)	N2-C19	1.471(18)	N2-C20	1.504(19)
N3-C21	1.485(18)	N3-C22	1.493(19)		
N1-Cu1-N2	84.6(5)	N2-Cu1-N3	83.7(5)	N3-Cu1-N4	94.3(5)
N4-Cu1-N1	91.9(5)	N5-Cu1-N1	98.4(5)	N5-Cu1-N2	98.1(5)
N5-Cu1-N3	94.9(5)	N5-Cu1-N4	104.4(5)	N1-Cu1-N3	163.4(4)
N2-Cu1-N4	157.5(5)				
PRT1					
Cu1-N1	2.133(4)	Cu1-N2	1.994(4)	Cu1-N3	2.137(4)
Cu1-N4	2.000(3)	Cu1-N5	2.115(4)	N1-C17	1.497(6)
N1-C18	1.479(6)	N2-C19	1.473(8)	N2-C20	1.448(8)
N3-C21	1.485(6)	N3-C22	1.456(8)		
N1-Cu1-N2	84.03(17)	N2-Cu1-N3	83.69(18)	N3-Cu1-N4	95.76(15)
N4-Cu1-N1	94.27(14)	N5-Cu1-N1	109.77(14)	N5-Cu1-N2	102.81(16)
N5-Cu1-N3	106.16(16)	N5-Cu1-N4	81.01(15)	N1-Cu1-N3	143.77(16)
N2-Cu1-N4	176.15(17)				
PRT2					
Cu1-N1	2.125(4)	Cu1-N2	2.014(4)	Cu1-N3	2.154(3)
Cu1-N4	2.020(3)	Cu1-N5	2.118(3)	N1-C17	1.492(6)
N1-C18	1.504(7)	N2-C19	1.471(7)	N2-C20	1.478(6)
N3-C21	1.489(7)	N3-C22	1.479(6)		
N1-Cu1-N2	82.75(15)	N2-Cu1-N3	82.36(14)	N3-Cu1-N4	94.40(12)
N4-Cu1-N1	99.02(13)	N5-Cu1-N1	111.24(13)	N5-Cu1-N2	103.11(14)
N5-Cu1-N3	109.94(13)	N5-Cu1-N4	79.05(13)	N1-Cu1-N3	138.37(13)
N2-Cu1-N4	176.55(14)				
PRT3					
Cu1-N1	2.081(3)	Cu1-N2	2.005(4)	Cu1-N3	2.137(3)
Cu1-N4	1.989(3)	Cu1-N5	2.169(3)	N1-C17	1.481(5)
N1-C18	1.481(8)	N2-C19	1.476(7)	N2-C20	1.461(6)
N3-C21	1.484(5)	N3-C22	1.479(5)	Cu2-N6	2.075(3)
Cu2-N7	2.016(3)	Cu2-N8	2.183(3)	Cu2-N9	1.985(3)
Cu2-N10	2.099(3)	N6-C57	1.503(6)	N6-C58	1.480(6)
N7-C59	1.487(6)	N7-C60	1.464(6)	N8-C61	1.475(5)
N8-C62	1.486(5)				
N1-Cu1-N2	83.40(13)	N2-Cu1-N3	82.73(12)	N3-Cu1-N4	96.08(11)
N4-Cu1-N1	97.64(12)	N5-Cu1-N1	109.31(12)	N5-Cu1-N2	101.16(13)
N5-Cu1-N3	105.16(11)	N5-Cu1-N4	79.06(11)	N1-Cu1-N3	144.69(11)
N2-Cu1-N4	178.81(13)	N6-Cu2-N7	84.82(14)	N7-Cu2-N8	83.09(13)
N8-Cu2-N9	96.06(11)	N9-Cu2-N6	97.36(12)	N10-Cu2-N6	127.86(12)
N10-Cu2-N7	97.24(13)	N10-Cu2-N8	102.44(11)	N10-Cu2-N9	80.82(11)
N6-Cu2-N8	129.34(12)	N7-Cu2-N9	177.69(13)		
PRT4					
Cu1-N1	2.154(8)	Cu1-N2	2.008(8)	Cu1-N3	2.169(8)
Cu1-N4	1.978(7)	Cu1-N5	2.103(8)	N1-C17	1.466(14)
N1-C18	1.496(15)	N2-C19	1.456(14)	N2-C20	1.472(15)
N3-C21	1.481(14)	N3-C22	1.49614)		

N1-Cu1-N2	83.7(3)	N2-Cu1-N3	83.2(3)	N3-Cu1-N4	96.9(3)
N4-Cu1-N1	98.0(3)	N5-Cu1-N1	119.6(3)	N5-Cu1-N2	97.8(3)
N5-Cu1-N3	119.5(3)	N5-Cu1-N4	80.4(3)	N1-Cu1-N3	120.6(3)
N2-Cu1-N4	178.0(3)				

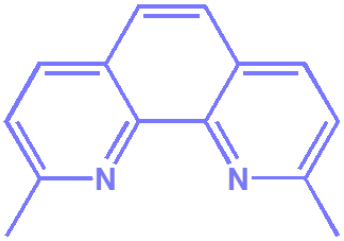


Chart 1S: Chemical Structure of **L5**.

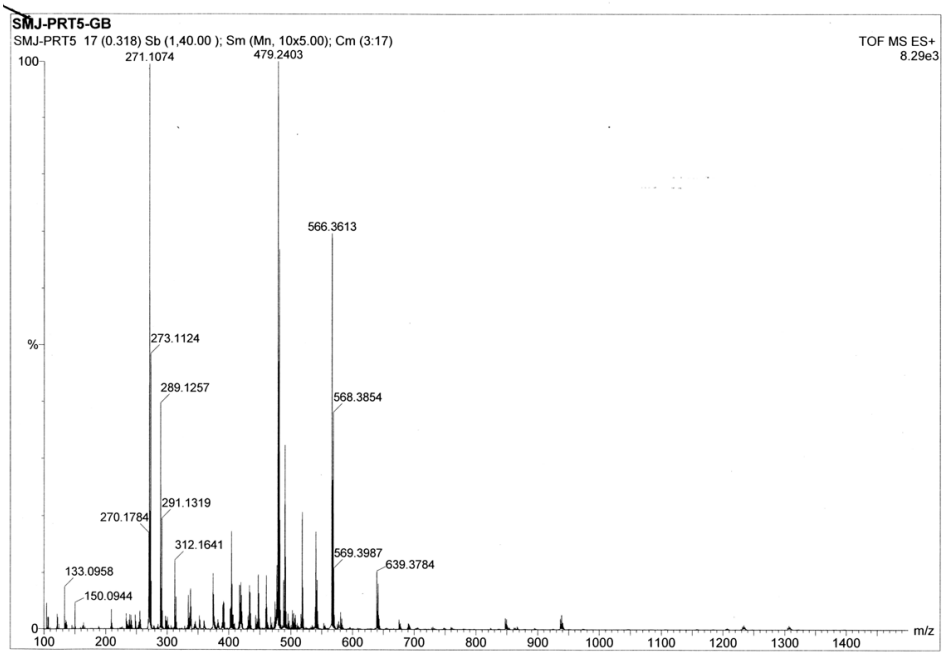


Figure 34S. ESI-MS spectrum of solution after mixing 1:1:1 of **MC**, $Cu(ClO_4)_2 \cdot 6H_2O$ and **L5**.

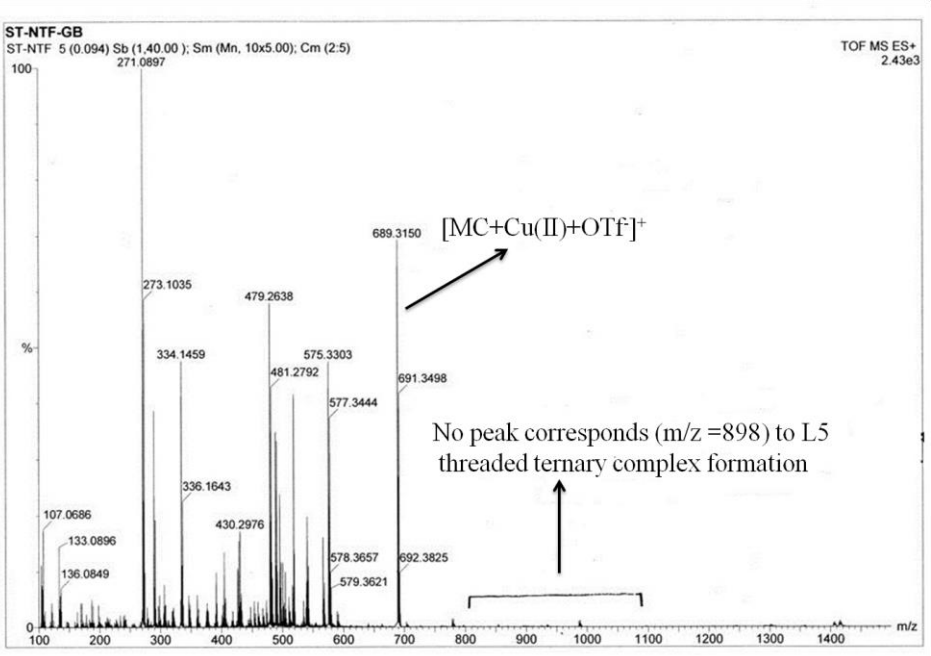


Figure 35S. ESI-MS spectrum of solution after mixing 1:1 of (**MC**)$Cu^{II}(OTf)_2$ and **L5**.

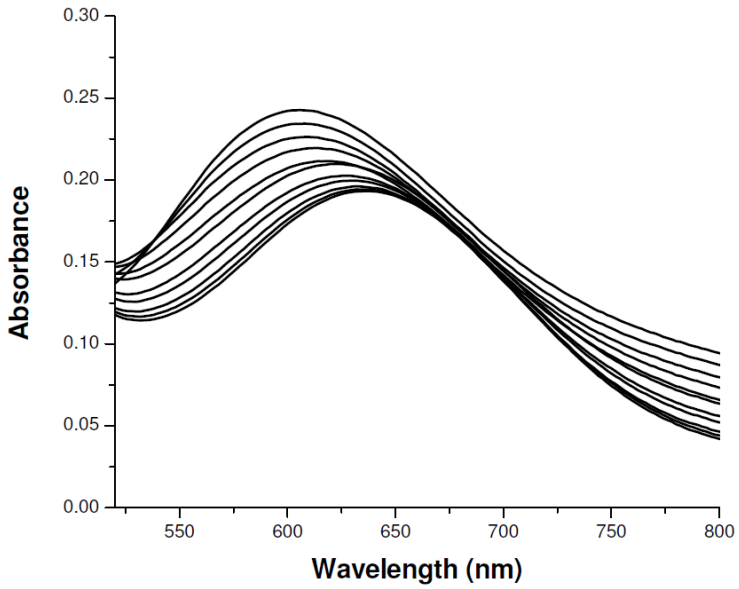


Figure 36S. UV/Vis spectra of the titration between mixing of 1:1 of (MC)$Cu^{II}(ClO_4)_2$ and **L5** in acetonitrile.

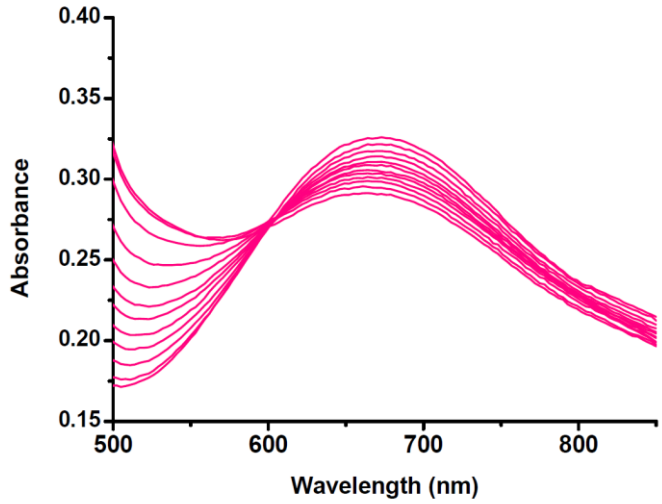
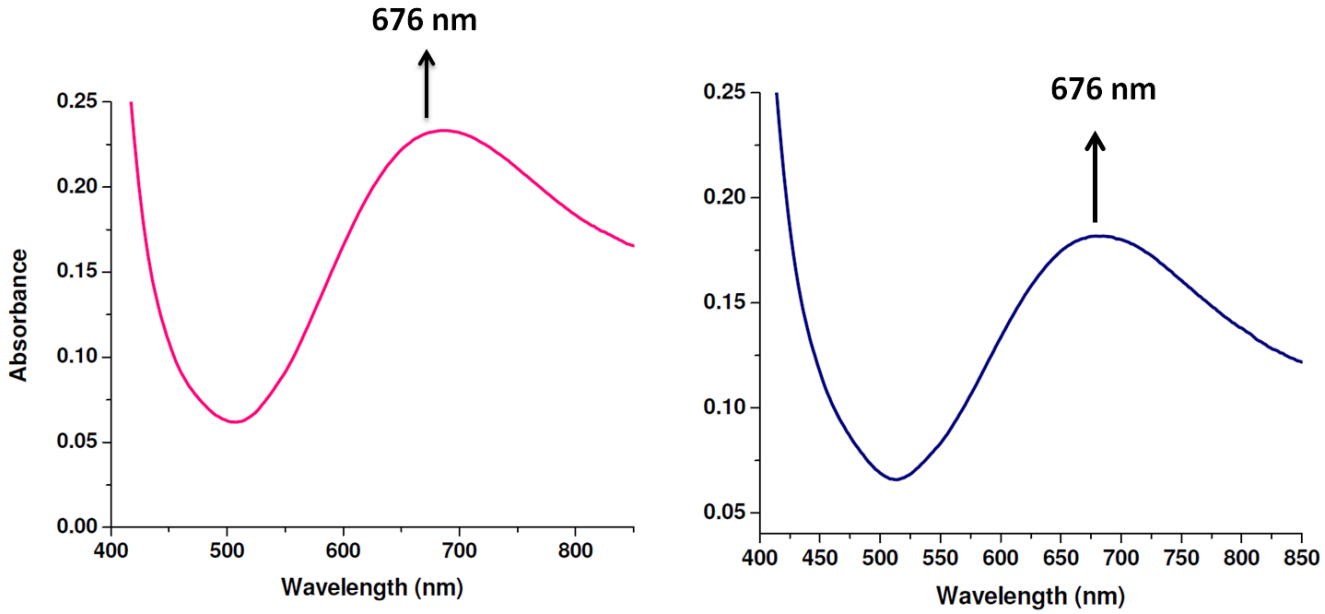


Figure 37S. (a) UV/Vis Spectrum the ligand substitution from **PRT3**·2ClO_4 by **L1**.



(i) (ii)

Figure 37S. (b) UV/Vis Spectrum the (i) solution containing equivalent amount of **MC**, **L1** and each of the transition metal ions (Cu^{II}, Co^{II}, Ni^{II} and Zn^{II}); (ii) solution containing equivalent amount of **MC**, **L1**-**L5** and each of the each of the transition metal ions (Cu^{II}, Co^{II}, Ni^{II} and Zn^{II}).

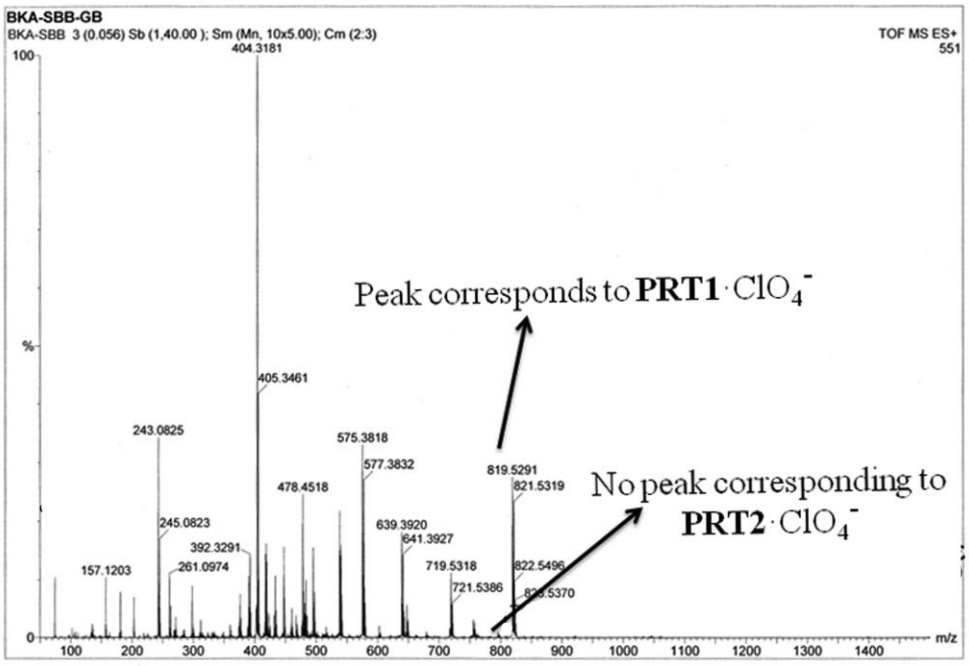


Figure 38S. ESI-MS spectrum of solution after titrating the solution of **PRT2**·$2ClO_4^-$ with **L1** in acetonitrile.

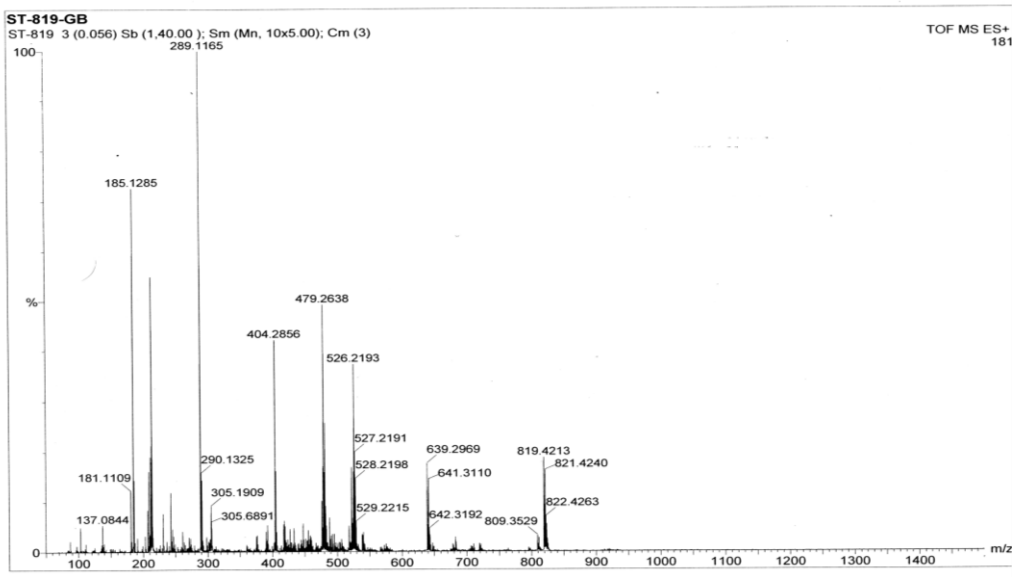


Figure 39S. ESI-MS spectrum of solution after titrating the solution of **PRT3**·$2ClO_4^-$ with **L1** in acetonitrile.

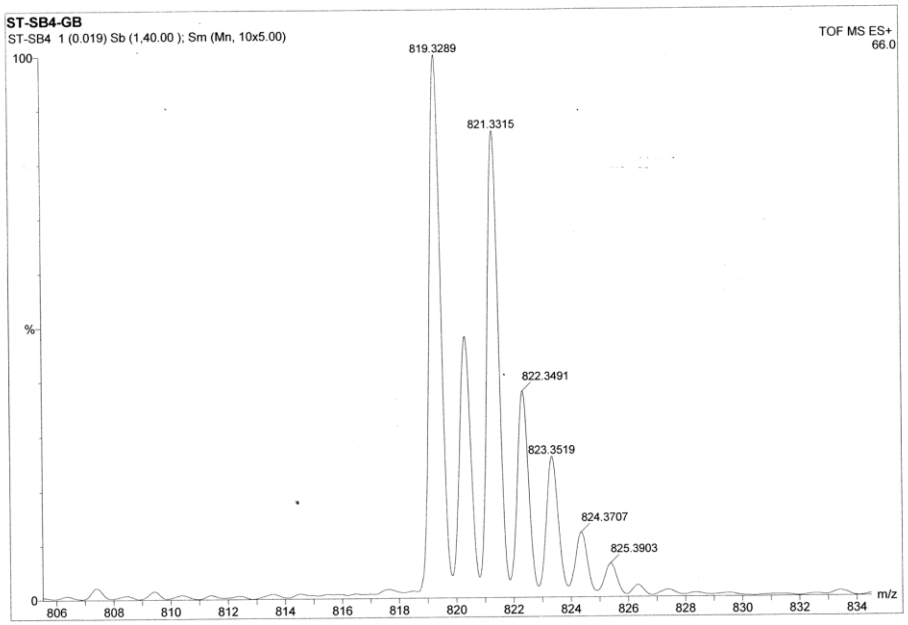


Figure 40S. ESI-MS spectrum of solution after titrating the solution of **PRT4**·$2ClO_4^-$ with **L1** in acetonitrile.

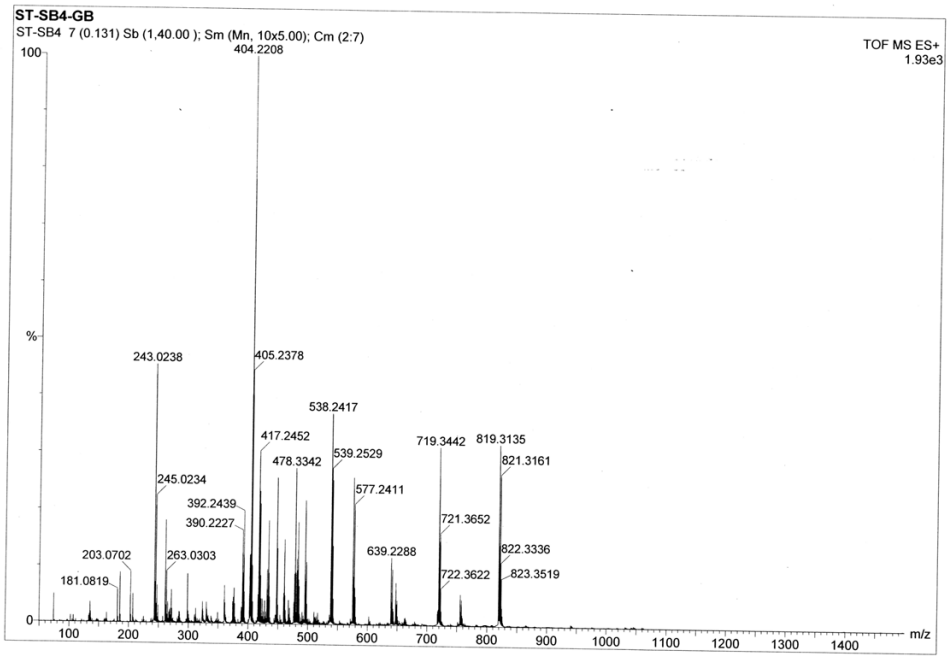


Figure 41S. ESI-MS spectrum of the isolated solid after mixing all the bidentate chelating ligands (**L1**-**L5**), four divalent transition metal ions and **MC** in equimolar amount.

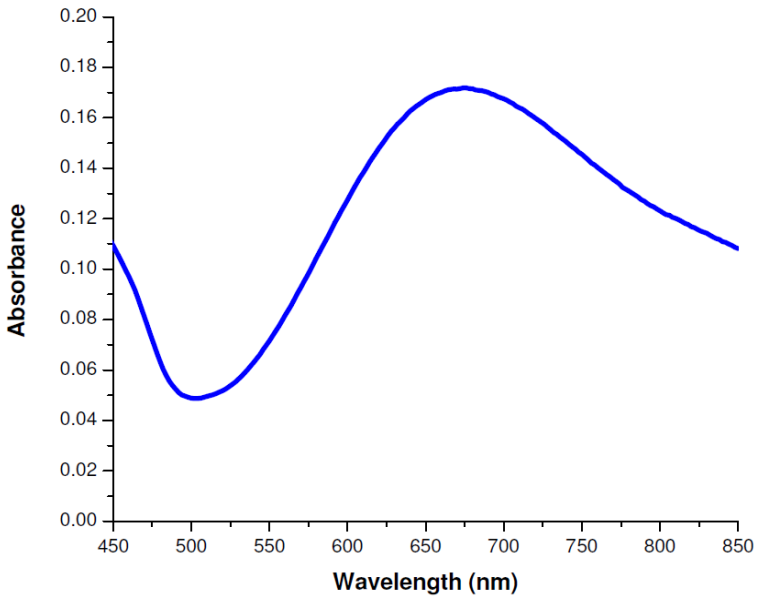


Figure 42S. UV/Vis spectra of the product isolated after mixing of all the bidentate chelating ligands (**L1**-**L5**), four divalent transition metal ions and **MC** in equivalent amount in acetonitrile.

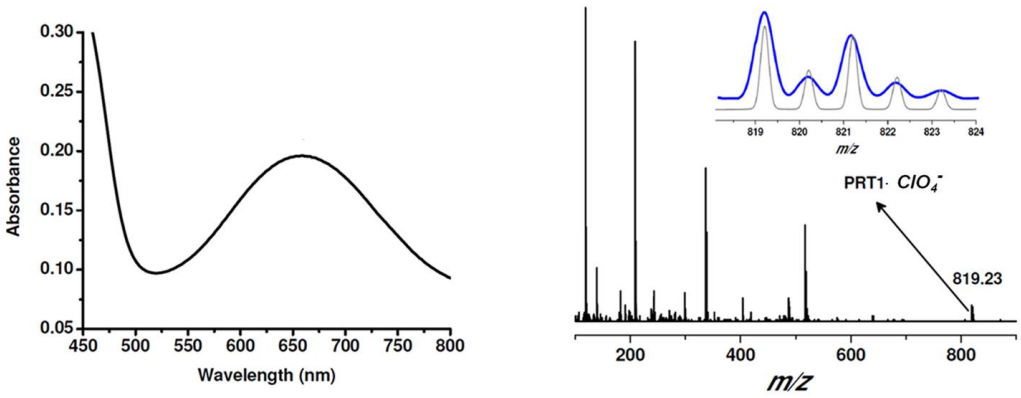
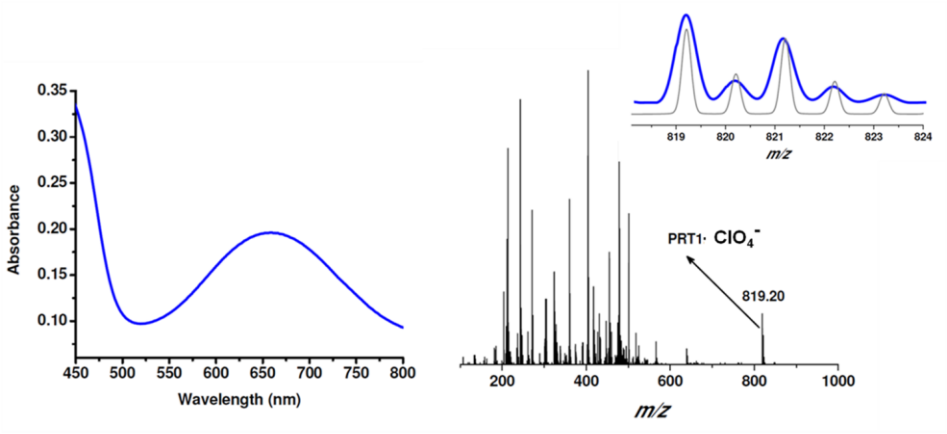


Fig. 43S (a) UV/Vis spectrum and (b) ESI-MS spectrum of the complex isolated from the mixture of 1:1 **MC**:Cu^{II} and equimolar mixture of each of the bidentate chelating ligands (**L1**-**L4**) in acetonitrile. [experimental and simulated ESI-MS (+ve mode) spectrum are shown in blue and gray colour respectively]



(a) (b)

Figure 44S (a) UV/Vis spectrum and (b) ESI-MS spectrum of the complex isolated from the mixture of 1:1 **MC**:**L1** and equimolar mixture of each of the divalent transition metal ion (Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}) in acetonitrile. [Experimental and simulated spectrum ESI-MS (+ve mode) are shown in blue and gray color respectively]

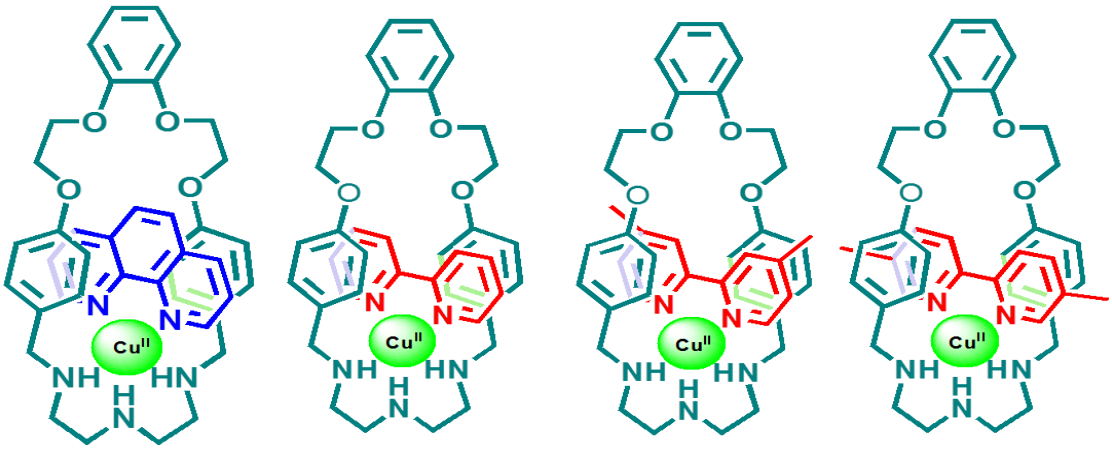


Chart2S. Possible ternary complexes for Guest ligand selectivity study.

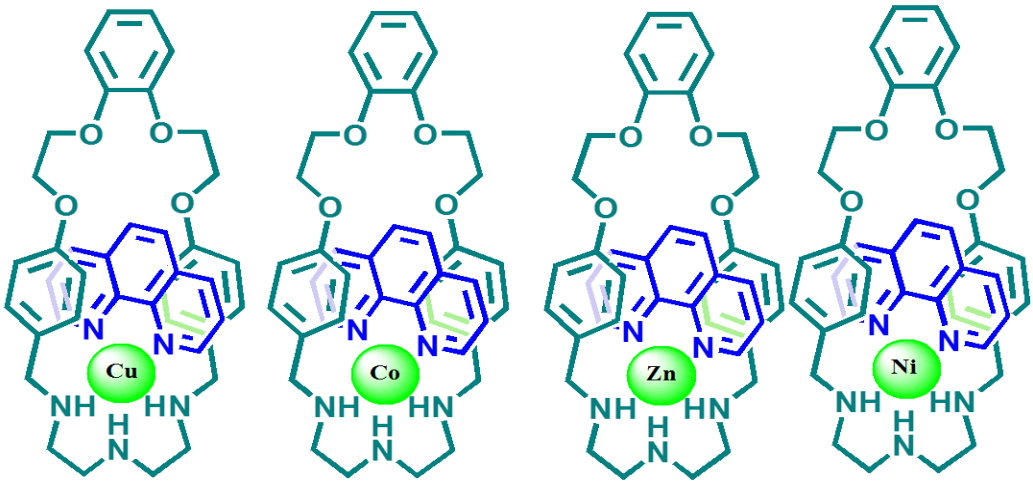


Chart3S. Possible ternary complexes for templating metal ion selectivity study.

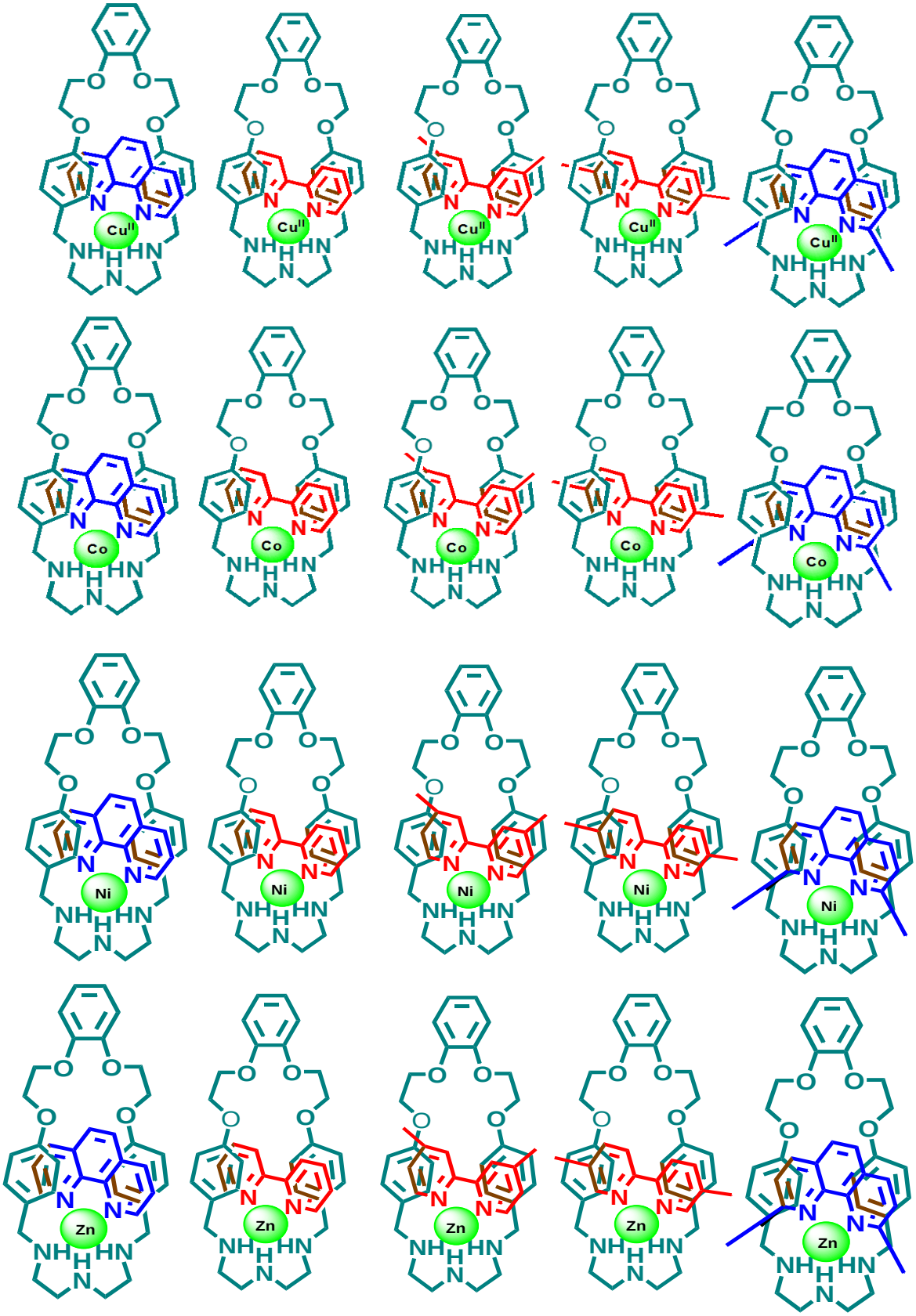
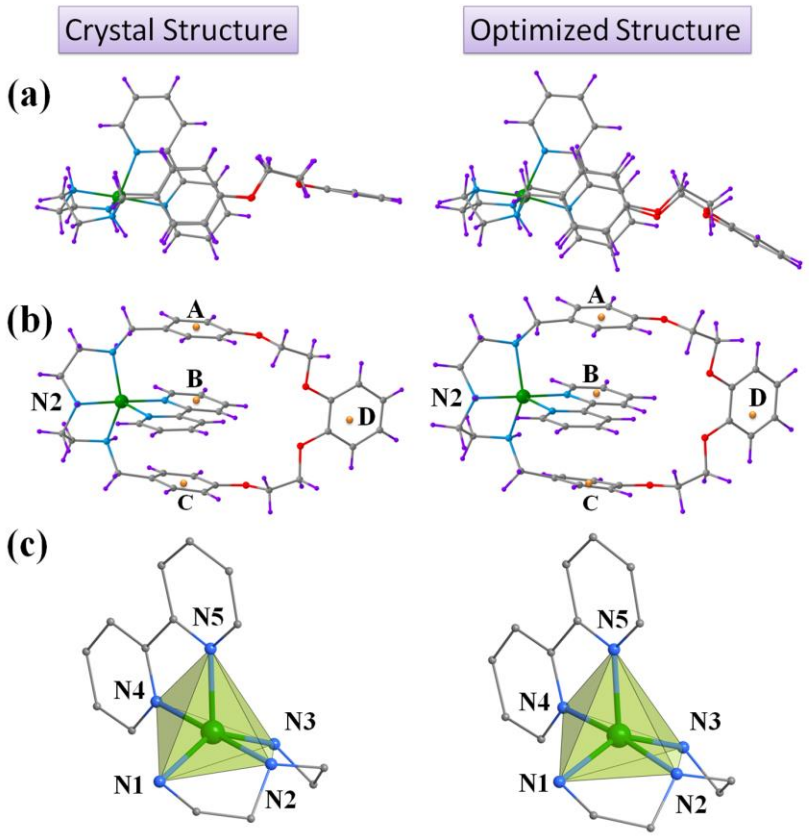
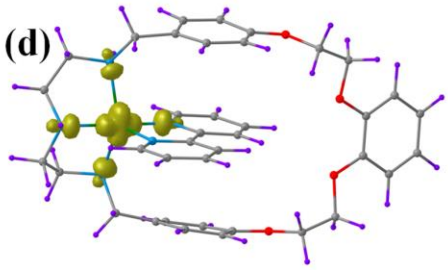


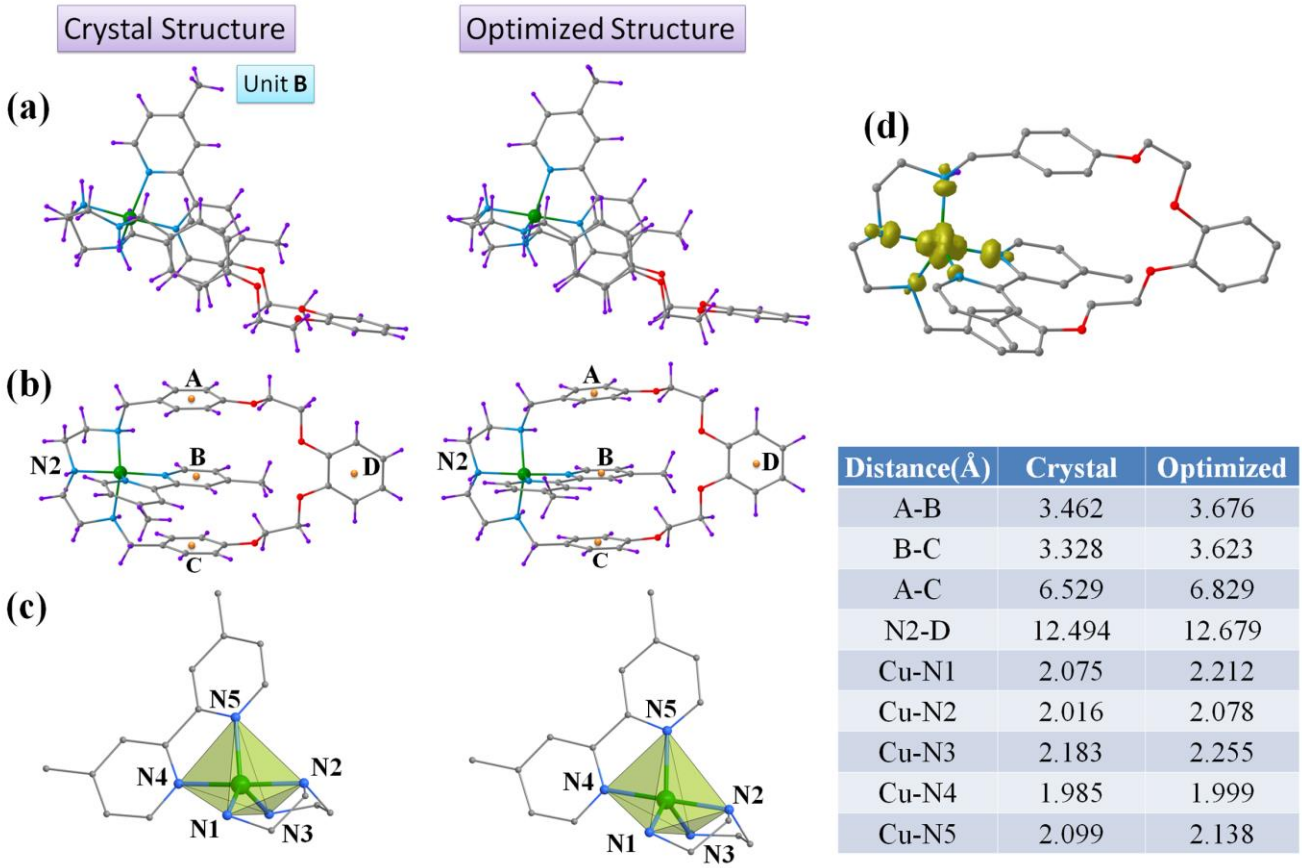
Chart4S. Possible ternary complexes for both Guest ligand and templating ion selectivity study.





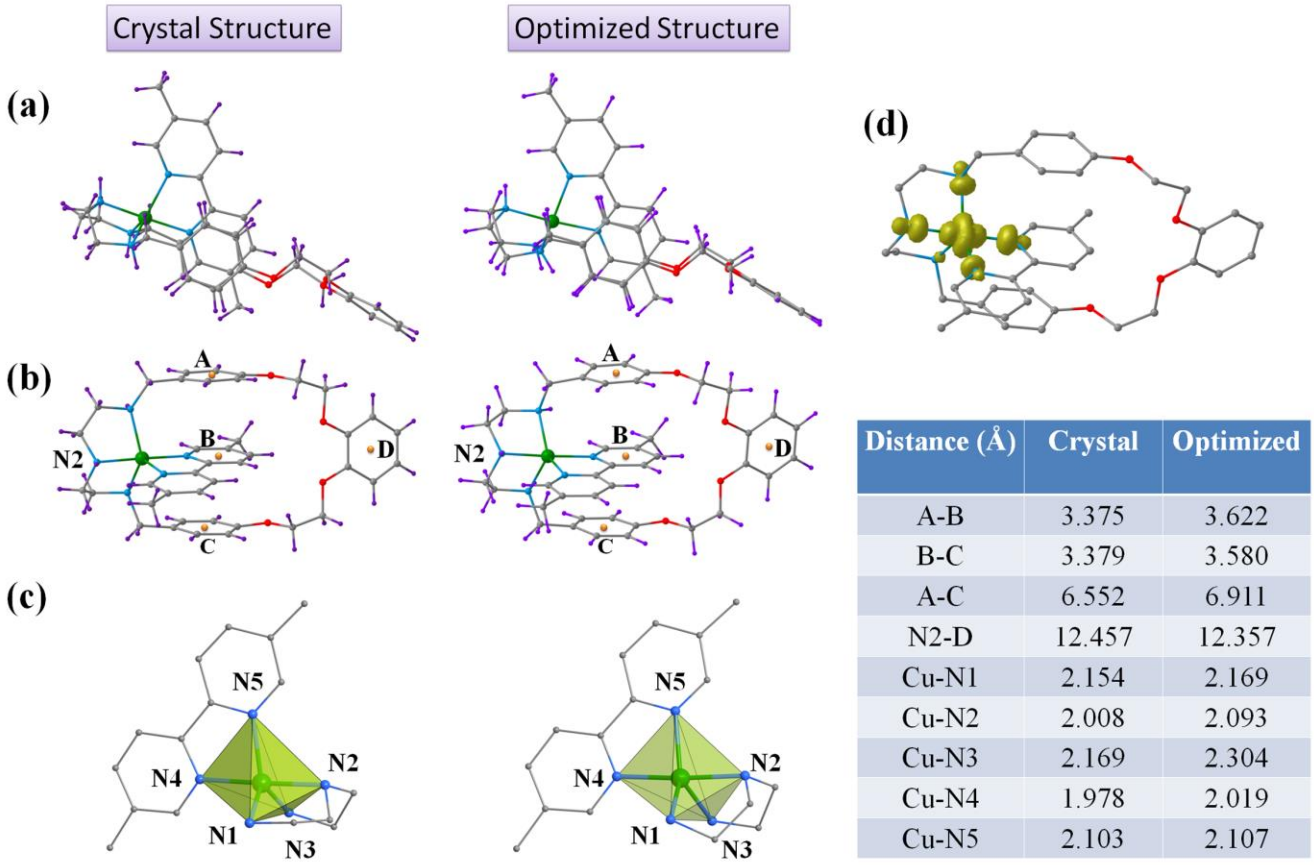
Distance(Å)	Crystal	Optimized
A-B	3.417	3.546
B-C	3.435	3.642
A-C	6.718	7.069
N2-D	12.248	12.344
Cu-N1	2.125	2.224
Cu-N2	2.014	2.078
Cu-N3	2.154	2.182
Cu-N4	2.020	2.019
Cu-N5	2.118	2.163

Figure 45S. Comparison between the crystal structure and the optimized structure for **PRT2** [Color Code: Green, Cu; Blue, N; Gray, C; Purple, H; Red, O; Orange, Centroid]. (a) Structural view perpendicular to the π-π stacking planes, (b) Structural view showing the centroids of the aromatic rings used for measuring important stacking distances, (c) View highlighting the coordination sphere of the copper ion, (d) Spin density map obtained from the analysis of the optimized structure showing that the unpaired electron resides in the $d_{(x^2-y^2)}$ orbital (supporting the experimental EPR results) of the Cu^{II} ion with the roughly square pyramidal geometry. The isodensity surfaces correspond to a value of 0.01 e/b^3.



Distance(Å)	Crystal	Optimized
A-B	3.462	3.676
B-C	3.328	3.623
A-C	6.529	6.829
N2-D	12.494	12.679
Cu-N1	2.075	2.212
Cu-N2	2.016	2.078
Cu-N3	2.183	2.255
Cu-N4	1.985	1.999
Cu-N5	2.099	2.138

Figure 46S. Comparison between the crystal structure and the optimized structure for **PRT3** [Color Code: Green, Cu; Blue, N; Gray, C; Purple, H; Red, O; Orange, Centroid]. (a) Structural view perpendicular to the π-π stacking planes, (b) Structural view showing the centroids of the aromatic rings used for measuring important stacking distances, (c) View highlighting the coordination sphere of the copper ion, (d) Spin density map (H atoms removed for clarity) obtained from the analysis of the optimized structure showing that the unpaired electron resides in an orbital best described as an linear combination of $d_{(x^2-y^2)}$ and d_{z^2} orbital (supporting the experimental EPR results) of the Cu^{II} ion with the roughly trigonal bipyramidal geometry. The isodensity surfaces correspond to a value of 0.01 e/b^3.



Distance (Å)	Crystal	Optimized
A-B	3.375	3.622
B-C	3.379	3.580
A-C	6.552	6.911
N2-D	12.457	12.357
Cu-N1	2.154	2.169
Cu-N2	2.008	2.093
Cu-N3	2.169	2.304
Cu-N4	1.978	2.019
Cu-N5	2.103	2.107

Figure 47S. Comparison between the crystal structure and the optimized structure for **PRT4** [Color Code: Green, Cu; Blue, N; Gray, C; Purple, H; Red, O; Orange, Centroid]. (a) Structural view perpendicular to the π-π stacking planes, (b) Structural view showing the centroids of the aromatic rings used for measuring important stacking distances, (c) View highlighting the coordination sphere of the copper ion, (d) Spin density map (H atoms removed for clarity) obtained from the analysis of the optimized structure showing that the unpaired electron resides in an orbital best described as an linear combination of $d_{(x^2-y^2)}$ and d_{z^2} orbital (supporting the experimental EPR results) of the Cu^{II} ion with the roughly trigonal bipyramidal geometry. The isodensity surfaces correspond to a value of 0.01 e/b^3.

Table 2S. Mulliken Atomic Spin-Densities (in au).

Atoms	**PRT1**	**PRT2**	**PRT3**	**PRT4**
Cu1	0.543169	0.496678	0.518941	0.573335
N1	0.105075	0.084891	0.076622	0.087739
N2	0.112033	0.109067	0.110948	0.119906
N3	0.090990	0.098968	0.057206	0.025895
N4	0.103096	0.106742	0.114045	0.123844
N5	0.010462	0.013574	0.045048	0.072223

Initial Geometry of MC (part of PRT1, Conf. I)

DFT/B3LYP/631g(d)

Energy = -1553.0894346 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	3.909312	-1.341794	-0.477912
2	6	0	0.409116	-3.412759	0.132038
3	6	0	-1.838426	-3.359106	-0.797476
4	1	0	-2.481533	-3.383882	-1.678048
5	6	0	5.193139	0.638623	0.030319
6	6	0	-0.140938	-3.471456	1.431080
7	1	0	0.535878	-3.542083	2.276739
8	6	0	-0.163376	3.460963	1.524475
9	1	0	0.404789	3.494361	2.448780
10	6	0	5.147674	-0.772665	-0.123150
11	6	0	-0.444891	-3.396956	-0.992786
12	1	0	-0.045310	-3.430634	-2.001226
13	6	0	-6.707174	-0.939212	-0.482090
14	1	0	-6.380042	-0.681801	-1.495157
15	1	0	-7.798730	-1.056321	-0.508334
16	6	0	-3.892638	-3.236143	0.721473
17	1	0	-4.386989	-4.145853	0.341538
18	1	0	-4.113264	-3.167861	1.791550
19	6	0	-1.525877	-3.411369	1.605065
20	1	0	-1.934823	-3.441169	2.613234
21	6	0	0.541534	3.469214	0.300369
22	6	0	2.487083	-3.149700	-1.192020
23	1	0	2.002385	-2.351742	-1.770166
24	1	0	2.473487	-4.086429	-1.765871
25	6	0	-2.397480	-3.318972	0.496646
26	6	0	-6.036103	-2.230619	-0.019341
27	1	0	-6.381219	-2.503284	0.985677
28	1	0	-6.309700	-3.058298	-0.689612
29	6	0	-2.285850	3.327371	0.316818
30	6	0	-1.559362	3.378714	1.526534
31	1	0	-2.087787	3.352874	2.477697
32	6	0	6.317798	-1.527345	0.080100
33	1	0	6.309314	-2.604297	-0.046007
34	6	0	-1.574626	3.446431	-0.896570
35	1	0	-2.109675	3.506030	-1.844992
36	6	0	3.912830	-2.756344	-0.856555
37	1	0	4.273826	-3.382228	-0.030102
38	1	0	4.561892	-2.902451	-1.732152
39	6	0	6.402276	1.258318	0.394552
40	1	0	6.454222	2.334818	0.517098
41	6	0	-0.171101	3.513071	-0.918958
42	1	0	0.343632	3.610379	-1.868747
43	6	0	-5.528023	1.952283	-1.093695
44	1	0	-5.718945	2.966549	-1.469456
45	1	0	-5.532720	1.281236	-1.960468
46	6	0	7.566007	0.493493	0.603198
47	1	0	8.491211	0.988510	0.882288
48	6	0	-3.789411	3.142355	0.312964
49	1	0	-4.178824	3.101813	1.334616
50	1	0	-4.282116	3.982390	-0.200542
51	6	0	-6.624821	1.554457	-0.102171
52	1	0	-7.610934	1.569631	-0.585395
53	1	0	-6.652532	2.257191	0.737665
54	6	0	4.115010	2.801862	-0.369004
55	1	0	4.859454	3.024486	-1.146885
56	1	0	4.418173	3.283540	0.569895
57	6	0	7.523891	-0.897889	0.443560
58	1	0	8.416850	-1.496891	0.594751
59	6	0	2.755375	3.320133	-0.795598
60	1	0	2.844759	4.320930	-1.238981
61	1	0	2.312696	2.626656	-1.521584
62	7	0	-4.188525	1.859908	-0.422804
63	7	0	-4.548055	-2.040953	0.046330
64	7	0	-6.314985	0.183715	0.442653
65	8	0	1.791369	-3.356145	0.084455

66	8	0	1.919663	3.408660	0.410607
67	8	0	3.999590	1.350965	-0.199014
68	1	0	-6.807666	0.052056	1.331241
69	1	0	-4.174279	-1.981204	-0.908791
70	1	0	-3.463828	1.690281	-1.127262

Optimized Geometry of MC (Conf. III)

DFT/B3LYP/631g(d)

Energy = -1553.1302307 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	4.264591	1.033985	0.759388
2	6	0	0.682646	2.804224	-0.087779
3	6	0	-1.421526	3.468176	0.891334
4	1	0	-1.970925	3.864777	1.742612
5	6	0	5.311157	-0.942691	0.032757
6	6	0	0.004062	2.465317	-1.269977
7	1	0	0.581407	2.079283	-2.104684
8	6	0	-0.632611	-1.413423	-0.666015
9	1	0	-0.160956	-0.519820	-1.061805
10	6	0	5.401599	0.449732	0.283864
11	6	0	-0.035769	3.309010	0.999207
12	1	0	0.461392	3.580132	1.923656
13	6	0	-6.477801	0.958955	0.132711
14	1	0	-6.079577	0.742142	1.131660
15	1	0	-7.551667	1.201884	0.271019
16	6	0	-3.609672	3.319370	-0.368815
17	1	0	-3.951505	3.921653	0.497014
18	1	0	-3.860719	3.910438	-1.262120
19	6	0	-1.372233	2.628373	-1.355069
20	1	0	-1.890575	2.354083	-2.270125
21	6	0	0.184993	-2.473409	-0.243052
22	6	0	2.770235	2.846028	1.086916
23	1	0	2.363816	2.251667	1.915749
24	1	0	2.730855	3.909967	1.365505
25	6	0	-2.112040	3.138365	-0.274931
26	6	0	-5.769848	2.203570	-0.399775
27	1	0	-6.157630	2.460310	-1.398752
28	1	0	-6.057846	3.043584	0.262818
29	6	0	-2.617274	-2.677046	-0.055294
30	6	0	-2.012885	-1.516019	-0.568284
31	1	0	-2.641797	-0.689514	-0.891243
32	6	0	6.600420	1.115933	0.036654
33	1	0	6.682269	2.178504	0.236591
34	6	0	-1.790903	-3.710178	0.384557
35	1	0	-2.235890	-4.616159	0.791882
36	6	0	4.209836	2.449349	0.830426
37	1	0	4.552997	2.900343	-0.110065
38	1	0	4.844038	2.822675	1.648911
39	6	0	6.414247	-1.618443	-0.485103
40	1	0	6.350937	-2.680627	-0.693568
41	6	0	-0.396028	-3.620836	0.303266
42	1	0	0.211718	-4.447883	0.653212
43	6	0	-6.155396	-1.961304	1.096470
44	1	0	-6.547818	-2.982490	1.278973
45	1	0	-6.459012	-1.356729	1.959756
46	6	0	7.611825	-0.935993	-0.740060
47	1	0	8.460605	-1.480419	-1.143745
48	6	0	-4.123116	-2.788654	0.002352
49	1	0	-4.537166	-2.481042	-0.963800
50	1	0	-4.410558	-3.848411	0.151459
51	6	0	-6.856239	-1.439835	-0.174632
52	1	0	-7.933926	-1.341358	0.070242
53	1	0	-6.789280	-2.197096	-0.964306
54	6	0	3.841566	-2.810497	-0.182019
55	1	0	4.527429	-3.559317	0.242713
56	1	0	3.958384	-2.813342	-1.274522
57	6	0	7.705887	0.423087	-0.475816

58	1	0	8.630557	0.960296	-0.666093
59	6	0	2.425437	-3.197802	0.193478
60	1	0	2.253342	-4.228561	-0.151662
61	1	0	2.299068	-3.173084	1.284983
62	7	0	-4.698809	-1.902179	1.017672
63	7	0	-4.319089	2.043614	-0.474535
64	7	0	-6.262810	-0.215916	-0.697907
65	8	0	2.035683	2.614339	-0.105308
66	8	0	1.530269	-2.293343	-0.427267
67	8	0	4.111181	-1.518758	0.335999
68	1	0	-6.615779	-0.037622	-1.635751
69	1	0	-4.005848	1.405827	0.255431
70	1	0	-4.302585	-2.142675	1.924727

Optimized Geometry of PRT1

DFT/B3LYP/LanL2DZ

Energy = -2320.20804522 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	3.417476	-0.006733	-0.421862
2	8	0	-4.590512	-1.342318	0.220271
3	6	0	-0.426542	-3.651061	-1.384501
4	1	0	-1.003679	-3.796970	-2.292053
5	8	0	-2.496616	-3.471596	-0.265021
6	6	0	0.401381	0.002901	2.692354
7	6	0	1.233412	0.008923	1.534112
8	6	0	-0.251175	3.635622	-1.410069
9	1	0	-0.766013	3.752580	-2.358523
10	6	0	1.009259	-3.335519	1.004495
11	1	0	1.558081	-3.240244	1.939459
12	6	0	-1.117815	-3.524678	-0.157248
13	6	0	3.207980	-3.177069	-0.268447
14	1	0	3.697331	-4.089051	-0.646580
15	1	0	3.607679	-2.974576	0.729511
16	6	0	1.706024	-3.360262	-0.216282
17	6	0	-5.739475	0.714706	-0.329215
18	6	0	-4.686904	-2.790014	0.447258
19	1	0	-4.955413	-3.308818	-0.481381
20	1	0	-5.454080	-2.987351	1.209477
21	6	0	-0.393778	-3.433098	1.049521
22	1	0	-0.898500	-3.426749	2.009488
23	6	0	0.967901	-3.578483	-1.406303
24	1	0	1.478772	-3.706246	-2.361415
25	6	0	1.143076	3.577402	-1.335485
26	1	0	1.717245	3.683229	-2.256490
27	6	0	-1.024493	3.532553	-0.230783
28	6	0	-5.758816	-0.702600	-0.249202
29	6	0	-6.920150	-1.400354	-0.629547
30	1	0	-6.962037	-2.481620	-0.567311
31	6	0	-0.385220	3.477569	1.024749
32	1	0	-0.952521	3.488331	1.948819
33	6	0	-6.878752	1.397452	-0.793507
34	1	0	-6.886668	2.479326	-0.860694
35	6	0	5.949446	-1.529414	-0.595383
36	1	0	5.894256	-2.110312	0.330979
37	1	0	6.995403	-1.532541	-0.928695
38	6	0	6.009465	0.903512	-1.264773
39	1	0	5.751339	0.586756	-2.281396
40	1	0	7.104309	0.973990	-1.206987
41	6	0	3.299731	3.256346	-0.009820
42	1	0	3.792504	4.186215	-0.338829
43	1	0	3.608572	3.069055	1.023146
44	6	0	-3.307501	3.349365	0.716610
45	1	0	-3.432230	4.346788	1.159149
46	1	0	-2.911781	2.658291	1.469871
47	6	0	1.797641	3.396235	-0.093285
48	6	0	-3.338304	-3.293607	0.925119
49	1	0	-2.889510	-2.570316	1.615838

50	1	0	-3.450398	-4.264070	1.427003
51	6	0	-4.635317	2.835311	0.194201
52	1	0	-5.438952	3.096850	0.896909
53	1	0	-4.843849	3.291361	-0.781749
54	6	0	5.035714	-2.137952	-1.662913
55	1	0	5.136874	-1.598837	-2.612250
56	1	0	5.320672	-3.182291	-1.848884
57	6	0	-8.033305	0.689729	-1.177996
58	1	0	-8.902684	1.234275	-1.533461
59	6	0	5.369409	2.248880	-0.928296
60	1	0	5.676739	3.012887	-1.654637
61	1	0	5.715024	2.586711	0.056237
62	6	0	1.017553	3.393854	1.076963
63	1	0	1.501852	3.327590	2.049426
64	6	0	-8.054295	-0.708244	-1.094706
65	1	0	-8.940752	-1.264692	-1.383356
66	7	0	5.486213	-0.126937	-0.299151
67	7	0	3.611187	-2.032787	-1.198135
68	7	0	3.868316	2.122189	-0.860871
69	7	0	1.443679	0.068034	-0.879141
70	7	0	2.607632	-0.023523	1.614596
71	6	0	-0.508118	0.087145	-2.309075
72	1	0	-0.900601	0.102806	-3.319765
73	6	0	0.625153	0.045024	0.225421
74	6	0	0.890428	0.089538	-2.108815
75	1	0	1.565000	0.112674	-2.960314
76	6	0	-0.793369	0.050462	0.103177
77	6	0	-1.356715	0.068806	-1.202125
78	1	0	-2.437444	0.073011	-1.309558
79	6	0	-1.614495	0.038506	1.291079
80	1	0	-2.694362	0.042652	1.157624
81	6	0	3.185867	-0.054787	2.830155
82	1	0	4.271310	-0.081255	2.867748
83	6	0	1.043693	-0.028225	3.962681
84	1	0	0.445639	-0.031831	4.870174
85	6	0	2.436103	-0.056059	4.033093
86	1	0	2.952855	-0.080862	4.986447
87	8	0	-4.555764	1.373010	0.074323
88	8	0	-2.393682	3.453847	-0.428659
89	6	0	-1.034210	0.021045	2.538078
90	1	0	-1.651339	0.016145	3.433156
91	1	0	2.977568	-2.062902	-2.002903
92	1	0	3.473665	2.217484	-1.804356
93	1	0	5.773777	0.138668	0.648983

Optimized Geometry of PRT2

DFT/B3LYP/LanL2DZ

Energy = -2243.98202231 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	-3.312374	-0.011626	-0.438381
2	6	0	1.079138	3.588193	-0.141744
3	6	0	0.324575	3.725623	-1.330459
4	1	0	0.854968	3.874629	-2.265782
5	6	0	1.243132	-3.572144	-0.063223
6	6	0	-0.984151	3.402536	1.128124
7	1	0	-1.485340	3.308899	2.089764
8	6	0	0.419331	3.495473	1.101516
9	1	0	0.972952	3.489732	2.034376
10	6	0	-0.923792	-3.344569	1.016190
11	1	0	-1.506701	-3.230687	1.928133
12	6	0	-1.574307	-3.384406	-0.229292
13	6	0	0.596134	-3.720992	-1.312529
14	1	0	1.205736	-3.890232	-2.194462
15	6	0	-0.794794	-3.634513	-1.387365
16	1	0	-1.272711	-3.773694	-2.357746
17	6	0	5.788089	0.738123	-0.266616
18	6	0	0.476403	-3.450502	1.114638

19	1	0	0.947350	-3.434261	2.092039
20	6	0	-1.743089	3.429174	-0.055139
21	6	0	4.773527	-2.750505	0.602232
22	1	0	5.525770	-2.882473	1.393068
23	1	0	5.073455	-3.324415	-0.283494
24	6	0	5.819674	-0.678085	-0.171341
25	6	0	3.340584	3.327262	0.832271
26	1	0	2.928180	2.581153	1.523587
27	1	0	3.457894	4.288107	1.351052
28	6	0	-1.069259	3.654808	-1.280574
29	1	0	-1.629689	3.784461	-2.207036
30	6	0	6.994100	-1.367995	-0.525094
31	1	0	7.044526	-2.448320	-0.450656
32	6	0	8.095649	0.727428	-1.077832
33	1	0	8.965411	1.276691	-1.425126
34	6	0	4.675415	2.842096	0.299734
35	1	0	4.893788	3.348152	-0.649181
36	1	0	5.472059	3.066996	1.022855
37	6	0	3.420921	-3.246684	1.076850
38	1	0	3.531580	-4.171386	1.658706
39	1	0	2.936696	-2.477419	1.692280
40	6	0	6.927835	1.427351	-0.719962
41	1	0	6.924122	2.508716	-0.799139
42	6	0	8.129009	-0.669485	-0.978858
43	1	0	9.025673	-1.219971	-1.246847
44	6	0	-5.792073	-1.565309	-0.902280
45	1	0	-5.815559	-2.176588	0.005843
46	1	0	-6.801384	-1.571814	-1.333916
47	6	0	-5.247349	2.229487	-1.055906
48	1	0	-5.659508	2.522084	-0.082475
49	1	0	-5.520177	3.018626	-1.769302
50	6	0	-3.243600	3.254962	-0.012733
51	1	0	-3.578695	3.044717	1.007660
52	1	0	-3.749115	4.176868	-0.344251
53	6	0	-5.841836	0.890626	-1.487298
54	1	0	-5.500611	0.611883	-2.490548
55	1	0	-6.938588	0.947452	-1.513756
56	6	0	-4.770949	-2.125385	-1.895991
57	1	0	-4.790521	-1.555882	-2.832802
58	1	0	-5.020120	-3.166634	-2.141520
59	6	0	-0.593939	0.037493	0.530104
60	6	0	-1.385308	-0.013346	1.787063
61	6	0	-0.650282	0.129724	-1.826715
62	1	0	-1.257623	0.178464	-2.726009
63	6	0	0.748393	0.115439	-1.911261
64	1	0	1.232091	0.148810	-2.881253
65	6	0	0.812049	0.023050	0.501834
66	1	0	1.382614	-0.024051	1.421245
67	6	0	-3.531165	-0.137022	2.752963
68	1	0	-4.604394	-0.193155	2.595168
69	6	0	1.498866	0.061208	-0.722523
70	1	0	2.585349	0.052795	-0.726805
71	6	0	-3.007883	-0.126837	4.055162
72	1	0	-3.671201	-0.174441	4.912016
73	6	0	-1.610572	-0.052017	4.209538
74	1	0	-1.166439	-0.037730	5.200252
75	7	0	-1.306098	0.090067	-0.638224
76	7	0	-2.746192	-0.081022	1.647709
77	8	0	2.449735	3.519550	-0.319730
78	8	0	2.623549	-3.533299	-0.122184
79	8	0	4.592525	1.389028	0.108960
80	8	0	4.650065	-1.324263	0.282456
81	7	0	-5.383360	-0.166906	-0.517623
82	7	0	-3.399221	-2.016609	-1.295361
83	7	0	-3.752653	2.119079	-0.899578
84	6	0	-3.069172	-3.173262	-0.349659
85	1	0	-3.558281	-4.073648	-0.754424
86	1	0	-3.511139	-2.964462	0.628971
87	6	0	-0.795475	0.005401	3.067214
88	1	0	0.280040	0.067227	3.179193
89	1	0	-2.692005	-2.025978	-2.036977
90	1	0	-3.305425	2.224672	-1.818438
91	1	0	-5.763493	0.058488	0.408035

Optimized Geometry of PRT3

DFT/B3LYP/LanL2DZ

Energy = -2322.62140813 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	3.311761	0.024253	-0.632891
2	8	0	-4.995738	1.341814	-0.504258
3	6	0	-1.460525	3.440671	-0.407437
4	6	0	0.598610	3.457207	-1.702817
5	1	0	1.083896	3.525796	-2.677189
6	6	0	-6.158696	-0.676081	0.131502
7	6	0	-0.699946	3.457460	0.781997
8	1	0	-1.225151	3.485028	1.731527
9	6	0	-0.603227	-3.472241	0.588235
10	1	0	-1.007202	-3.549996	1.592737
11	6	0	-6.151729	0.740614	0.030109
12	6	0	-0.808179	3.481370	-1.659473
13	1	0	-1.372255	3.547930	-2.584210
14	6	0	5.471247	1.101300	-2.308766
15	1	0	4.980273	0.878304	-3.262075
16	1	0	6.541736	1.235934	-2.513279
17	6	0	2.880381	3.306880	-0.556939
18	1	0	3.295895	4.238018	-0.977221
19	1	0	3.278749	3.200639	0.457171
20	6	0	0.694966	3.411773	0.718190
21	1	0	1.267688	3.408789	1.643668
22	6	0	-1.504242	-3.443882	-0.499317
23	6	0	-3.729590	3.197413	-1.373069
24	1	0	-3.342493	2.429874	-2.056415
25	1	0	-3.820846	4.155728	-1.902460
26	6	0	1.368070	3.375577	-0.523761
27	6	0	4.876813	2.363487	-1.687689
28	1	0	5.384027	2.602309	-0.744710
29	1	0	5.026508	3.220531	-2.360176
30	6	0	1.284172	-3.259771	-0.952466
31	6	0	0.772392	-3.368899	0.359024
32	1	0	1.453308	-3.371817	1.208116
33	6	0	-7.277233	1.468977	0.457625
34	1	0	-7.299266	2.550004	0.375797
35	6	0	0.379681	-3.342635	-2.032908
36	1	0	0.747740	-3.357369	-3.059382
37	6	0	-5.075024	2.769729	-0.819070
38	1	0	-5.296888	3.357624	0.081058
39	1	0	-5.863572	2.939688	-1.566468
40	6	0	-7.283856	-1.327724	0.668229
41	1	0	-7.305266	-2.408823	0.753871
42	6	0	-1.006928	-3.429710	-1.821818
43	1	0	-1.673510	-3.498043	-2.674765
44	6	0	4.230489	-1.781994	-2.830627
45	1	0	4.363964	-2.777949	-3.274068
46	1	0	4.083356	-1.077940	-3.657841
47	6	0	-8.402236	-0.589337	1.100399
48	1	0	-9.262940	-1.108797	1.510624
49	6	0	2.763955	-3.051885	-1.201399
50	1	0	3.319605	-3.044955	-0.258921
51	1	0	3.170194	-3.863841	-1.824135
52	6	0	5.475271	-1.406158	-2.022162
53	1	0	6.365944	-1.387629	-2.664434
54	1	0	5.650078	-2.140336	-1.228214
55	6	0	-5.144949	-2.805605	-0.530970
56	1	0	-6.007915	-3.009288	-1.181093
57	1	0	-5.281456	-3.327783	0.425141
58	6	0	-8.399440	0.807657	0.992683
59	1	0	-9.259204	1.386707	1.316016
60	6	0	-3.872295	-3.286243	-1.200697
61	1	0	-4.026617	-4.270392	-1.663090
62	1	0	-3.564192	-2.558558	-1.961931
63	7	0	1.446249	0.033046	0.085960
64	7	0	3.022468	-1.736023	-1.940990
65	7	0	3.422777	2.148801	-1.380667
66	7	0	3.735459	-0.138061	1.456736

67	7	0	5.250050	-0.062381	-1.377721
68	6	0	-2.506086	-0.052721	1.856141
69	1	0	-3.095896	-0.873910	1.428888
70	1	0	-3.050268	0.865466	1.597632
71	1	0	-2.483206	-0.156231	2.945160
72	6	0	3.968683	-0.338339	5.793430
73	1	0	4.439550	-1.277274	6.112674
74	1	0	2.983588	-0.278093	6.264821
75	1	0	4.585580	0.478098	6.189784
76	8	0	-2.830497	3.364911	-0.224329
77	8	0	-2.844549	-3.408615	-0.156692
78	8	0	-5.014858	-1.360777	-0.323919
79	6	0	2.588873	-0.127690	2.209563
80	6	0	4.932580	-0.214776	2.095913
81	1	0	5.827703	-0.227235	1.481521
82	6	0	3.882579	-0.267600	4.288148
83	6	0	5.050365	-0.280996	3.487302
84	1	0	6.034468	-0.342109	3.941633
85	6	0	2.645398	-0.189150	3.615143
86	1	0	1.730849	-0.175389	4.196661
87	6	0	1.317444	-0.053496	1.445732
88	6	0	-0.955025	0.057253	-0.145050
89	1	0	-1.822594	0.097446	-0.795339
90	6	0	0.045538	-0.079916	2.042777
91	1	0	-0.049642	-0.148110	3.120647
92	6	0	0.330628	0.090489	-0.685715
93	1	0	0.475705	0.170238	-1.756823
94	6	0	-1.125794	-0.026722	1.256748
95	1	0	5.884291	0.042304	-0.579951
96	1	0	2.893914	2.120346	-2.261024
97	1	0	2.188009	-1.550332	-2.506159

Optimized Geometry of PRT4

DFT/B3LYP/LanL2DZ

Energy = -2322.61702581 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	-3.095114	0.222324	-0.423979
2	8	0	2.502204	-3.280208	-0.886476
3	6	0	-4.196434	-0.443662	2.440613
4	8	0	4.658056	-1.498483	0.263628
5	8	0	4.784322	1.197250	0.647782
6	8	0	2.866865	3.421549	-0.052559
7	6	0	1.490584	3.547511	-0.144935
8	6	0	1.116953	-3.352883	-0.921155
9	6	0	4.897527	2.625908	0.963589
10	6	0	0.597375	3.461331	0.943942
11	6	0	7.094962	-1.587741	-0.180666
12	6	0	0.532991	-3.197120	-2.199224
13	6	0	-0.388531	3.724871	-1.677138
14	6	0	3.216563	-3.442699	0.385955
15	6	0	7.227430	1.180726	0.227969
16	6	0	5.920714	-0.878798	0.133339
17	6	0	0.990471	3.740384	-1.453543
18	6	0	-1.101810	-3.419681	0.069977
19	6	0	4.640534	-2.963658	0.180163
20	6	0	-1.297016	3.513521	-0.609544
21	6	0	5.987192	0.524974	0.337511
22	6	0	-3.185760	-2.949410	-1.308641
23	6	0	0.293603	-3.527731	0.210414
24	6	0	-1.694487	-3.168301	-1.179277
25	6	0	-0.857191	-3.112650	-2.321174
26	6	0	8.329800	-0.921397	-0.292784
27	6	0	3.507886	3.165347	1.243793
28	6	0	8.396174	0.462202	-0.087226
29	6	0	-0.747596	-0.114792	1.204090
30	6	0	-1.860425	-0.281965	2.161007
31	6	0	-0.151174	0.168510	-1.057832

32	6	0	1.228527	0.112982	-0.779495
33	6	0	-1.681164	-0.500758	3.542811
34	6	0	1.602098	-0.054177	0.574236
35	6	0	-2.793955	-0.691621	4.370118
36	6	0	-4.100292	-0.674293	3.825403
37	6	0	0.612574	-0.170673	1.559618
38	6	0	2.263618	0.221108	-1.867430
39	7	0	-1.107527	0.066872	-0.102962
40	7	0	-3.122400	-0.244792	1.630698
41	7	0	-5.160566	0.496715	-0.620359
42	7	0	-3.502359	-1.553587	-1.833529
43	7	0	-3.003075	2.009354	-1.649478
44	6	0	-2.768776	3.325698	-0.898985
45	6	0	-4.940089	-1.404399	-2.238323
46	6	0	-5.756314	-0.809197	-1.085085
47	6	0	-5.455911	1.690750	-1.501622
48	6	0	-5.327416	-0.892010	4.679707
49	6	0	-0.787183	3.432034	0.697866
50	6	0	-4.279381	1.994317	-2.436939
51	1	0	-5.177872	-0.432799	1.975955
52	1	0	5.533782	2.755031	1.850859
53	1	0	5.336383	3.173855	0.120169
54	1	0	0.958701	3.404781	1.965187
55	1	0	7.068580	-2.659610	-0.339740
56	1	0	1.184904	-3.141868	-3.065569
57	1	0	-0.757713	3.885664	-2.690083
58	1	0	3.211843	-4.506184	0.661797
59	1	0	2.737080	-2.855348	1.178827
60	1	0	7.304276	2.250178	0.386837
61	1	0	-1.729804	-3.533275	0.951836
62	1	0	5.286236	-3.381581	0.965758
63	1	0	5.001543	-3.298185	-0.800865
64	1	0	-3.629220	-3.681585	-2.002697
65	1	0	-3.679684	-3.070635	-0.339174
66	1	0	0.716343	-3.734164	1.187788
67	1	0	-1.288440	-3.016291	-3.317830
68	1	0	9.224242	-1.486770	-0.535805
69	1	0	3.570792	4.110084	1.800386
70	1	0	2.933828	2.432450	1.823917
71	1	0	9.343110	0.987216	-0.167218
72	1	0	-0.488712	0.290212	-2.081789
73	1	0	-0.685585	-0.525062	3.969360
74	1	0	2.660053	-0.100356	0.823764
75	1	0	-2.654406	-0.859173	5.434896
76	1	0	0.901697	-0.311831	2.594845
77	1	0	2.940326	1.059614	-1.662854
78	1	0	1.812365	0.362277	-2.855228
79	1	0	2.882692	-0.684074	-1.886298
80	1	0	-3.153192	4.139091	-1.533603
81	1	0	-3.355615	3.313176	0.024540
82	1	0	-5.005124	-0.763111	-3.123675
83	1	0	-5.376666	-2.372949	-2.519354
84	1	0	-6.370757	1.519731	-2.082699
85	1	0	-5.642636	2.550437	-0.848867
86	1	0	-5.294811	-1.871302	5.173406
87	1	0	-6.250304	-0.844917	4.092111
88	1	0	-5.395585	-0.135329	5.471327
89	1	0	-1.470317	3.340135	1.540741
90	1	0	-4.451364	2.957346	-2.938498
91	1	0	-4.192766	1.231897	-3.217292
92	1	0	1.697456	3.884237	-2.264519
93	1	0	-5.748416	-1.498936	-0.232825
94	1	0	-6.801877	-0.666644	-1.390725
95	1	0	-5.521374	0.702192	0.314569
96	1	0	-2.207795	1.894763	-2.286353
97	1	0	-2.897993	-1.397938	-2.646144