Supporting Information

for

The first examples of triply bonded dirhenium(II,II) complexes that contain bis(diphenylphosphino)methane and dithiocarbamato ligands: spectroscopic, structural, cytotoxicity and computational studies

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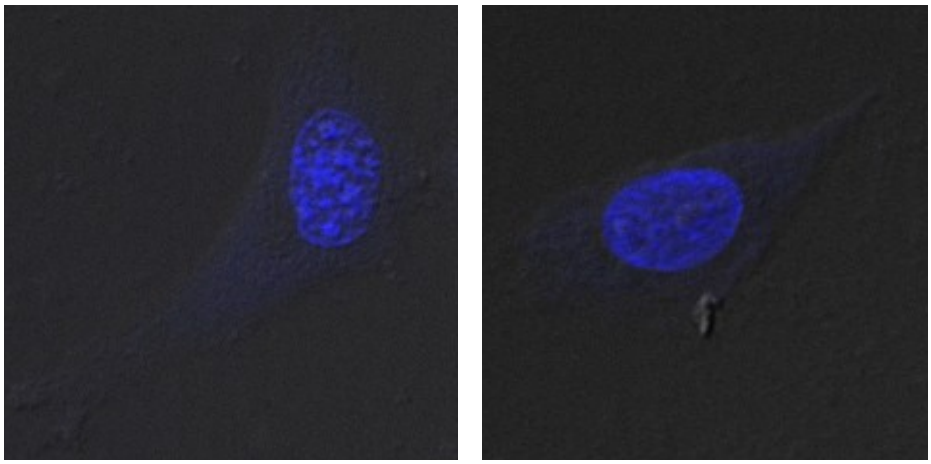
Contents of Supporting Information

MTT assay for cellular viability

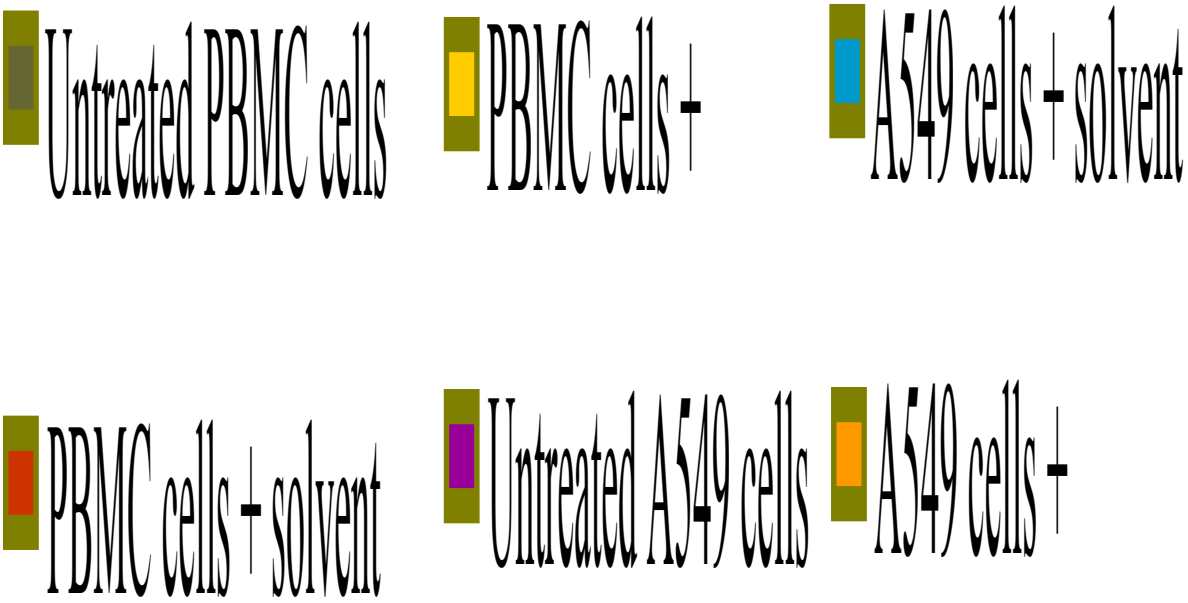
The % of viable cells after treatment with ligand L_{Et} were assessed using the lung cancer cell line A549 and normal peripheral blood mononuclear cells (PBMC) by MTT assay to the desired concentration range (10 µl – 60 µl, $[L_{Et}]$ = 0.63 µM/10µl). The result of solvent treated set served the standard to distinguish the effect of solvent on the cells in each case. Both the cells were incubated in 96-well microplates for 24h with or without the ligand L_{Et}. At the end of experimental time interval, MTT assay was performed by dissolving the intracellular formazan crystals formed in dimethyl sulfoxide (DMSO), the absorbance of the solution was measured at 595 nm using a microplate ELISA reader (Thermo Scientific, Multiscan Ex, Electron Corporation, USA). The % cell viability was calculated as: O.D of compound treated sample/O.D of untreated sample × 100. Additionally, confocal microscopic imaging was also performed using Hoescht dye for counterstaining the nucleus.

Results

The ligand L_{Et} was found to be non-toxic to both the normal PBMC and A549 lung cancer cells even after 96 h of incubation. Confocal images of PBMC and A549 cells showed no change in their morphology of cellular and nuclear membrane revealing that the ligand L_{Et} is non-toxic in nature.



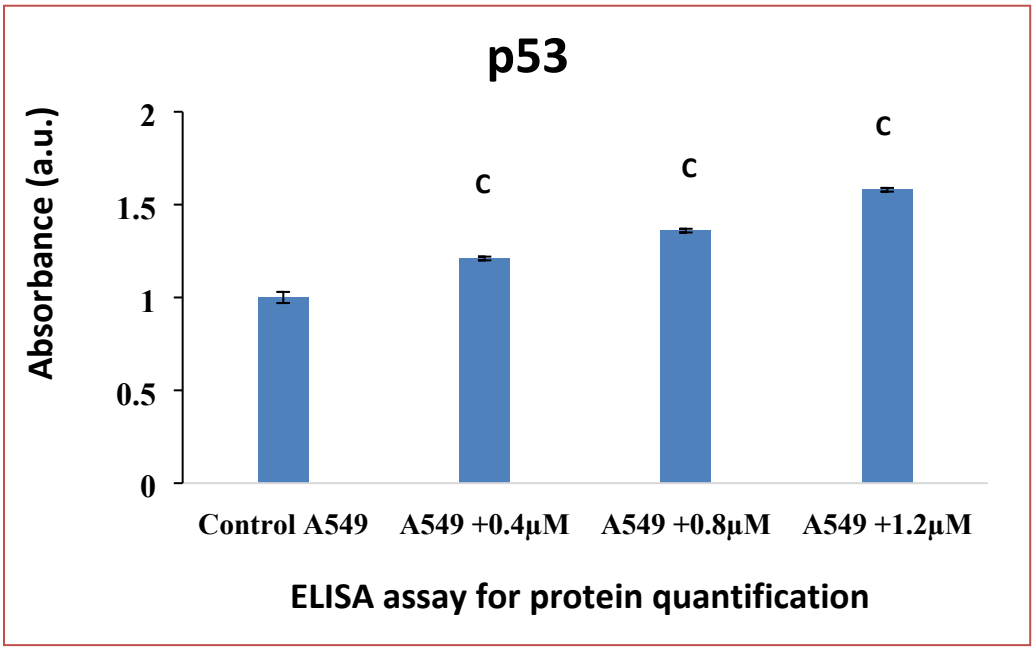
Confocal microscopic images of PBMC (left) and A549 cell (right) showing no change in their morphology of cellular membrane and nuclear orientation after counterstaining with Hoescht dye



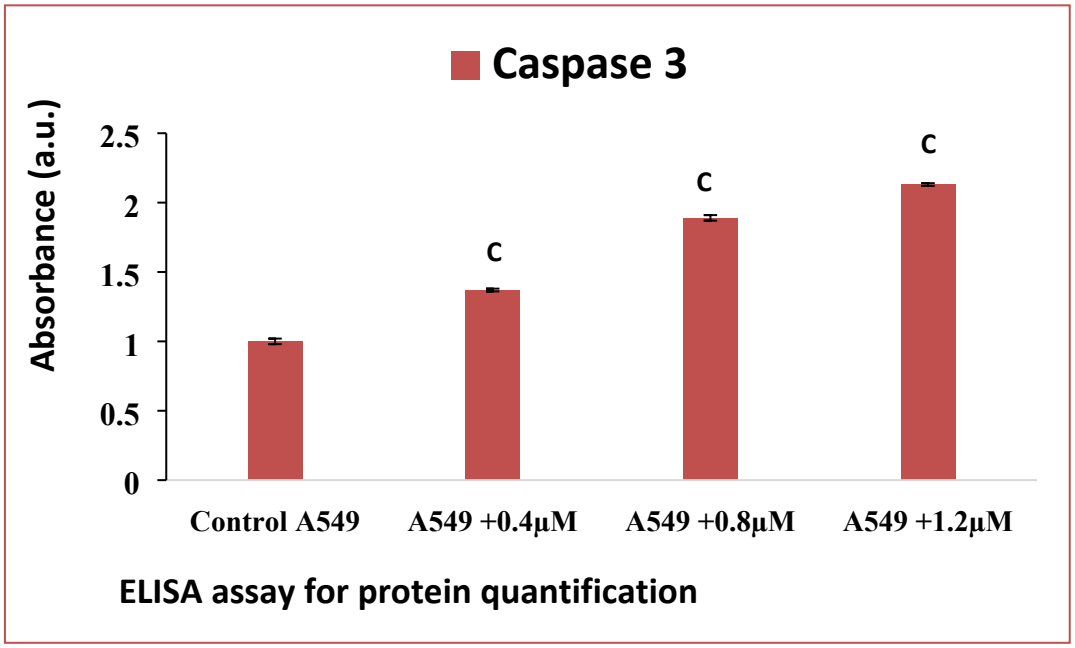
Indirect ELISA for quantifying proteins

The expressions of p53 and caspase 3 proteins were evaluated by using anti-p53 and anti-caspase 3 primary antibodies. The secondary antibodies that were used were of alkaline phosphatase conjugated. The standard protocols of indirect ELISA were adopted for determining any change in the cell cycle and apoptotic proteins p53 and caspase 3. The absorbance values were measured at 405 nm in an ELISA reader (Thermo Multiscan) connected with printer.

Result: The treatment of cancer cells A549 with the compound shows a significant increase of both the proteins revealing the ability of the compound to induce cell cycle arrest induced apoptosis of cancer cells.



Graphical representation of modulation of cell cycle and apoptotic protein p53 estimated by indirect ELISA. $^{c}p<0.001$ *vs* control were considered significant for Students' t-test.



Graphical representation of modulation of cell cycle and apoptotic protein caspase 3 estimated by indirect ELISA. $^{c}p<0.001$ *vs* control were considered significant for Students' t-test.

CT–DNA binding studies

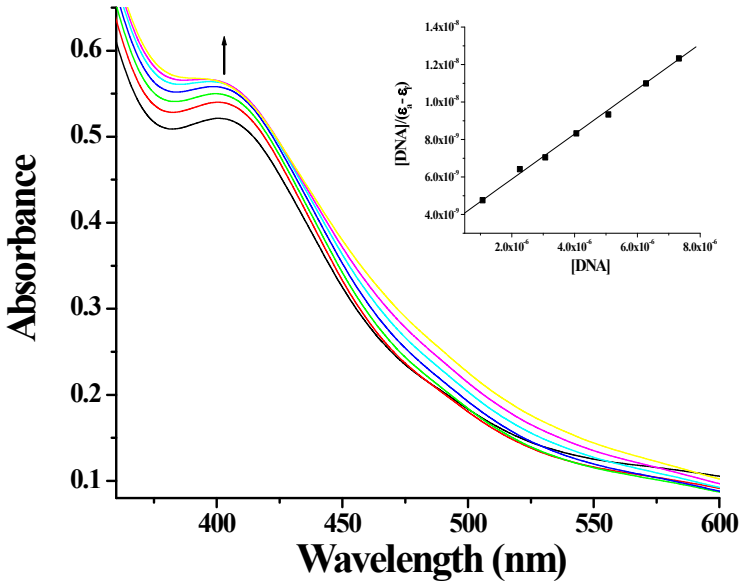
CT–DNA binding studies with the complex **2**(L_{Et}) was carried out by following a reported procedure.[1] The experiments were performed in Tris–HCl buffer (30 mM, pH 7.4). UV 7contamination. Further, concentration of CT-DNA solution was determined by absorption spectroscopy using the molar extinction coefficient of 13,600 $M^{-1}cm^{-1}$ at 260 nm.[2] Stock solution of the DNA were stored at 4 °C. The titration experiment was carried out by taking a fixed concentration of the complex **2**(L_{Et}) (6.67 x 10^{-5} M) with varying concentration of CT-DNA (0 - 7 μM) into a rectangular quartz cuvette having the path length of 1 cm. Equal amounts of CT-DNA solution were added to the complex solution and the reference solution to eliminate the absorbance of DNA itself. The reference solution was the same Tris-HCl buffer solution. After addition of DNA to the complex in Tris-HCl buffer, the resulting solution was allowed to equilibrate for 5 min at room temperature. Then, the solution was scanned in the specified wavelength window.

The binding affinity of the complex **2**(L_{Et}) for CT–DNA was evaluated using absorption measurements. It has been found that when metal complexes intercalate between DNA base pairs then there is generally a small red/blue shift causing a hypochromic effect, while non-intercalating/electrostatic or groove binding interactions give rise to a hyperchromic effect.[3] The UV-Vis spectra obtained during the titration of fixed concentration of **2**(L_{Et}) in the presence of increasing concentrations of CT-DNA are depicted in the figure below. Upon addition of increasing concentrations of DNA to the complex, the absorption spectra show 'hyperchromic' effect with a blue shift of ~4 nm of the absorption maximum of the complex. This hyperchromism accompanied by the blue shift is suggested to be generated through the active interactions of the complex with DNA base pairs. Quantitative affinity of the complex **2**(L_{Et}) for CT-DNA was judged from the intrinsic binding constant (K_b) value evaluated by monitoring the changes in absorbance at 400 nm with increasing concentrations of CT-DNA using eqn. (1) where, [DNA] is the concentration of DNA, ε_a is the ratio of the absorbance/[complex], ε_f is the extinction coefficient for free **2**(L_{Et}), and ε_b is the extinction coefficient for metal complex in the fully bound form.

$$[DNA] / (\varepsilon_a - \varepsilon_f) = [DNA] / (\varepsilon_b - \varepsilon_f) + 1/K_b (\varepsilon_b - \varepsilon_f) \text{ …….. (1)}$$

The value of K_b evaluated from the ratio of the slope to the intercept in the plot of $[DNA]/(\varepsilon_a - \varepsilon_f)$ vs. [DNA] was found to be 3.445 x 10^5 M^{-1}. Binding affinity measurements for CT–DNA with the ligand L_{Et} alone did not indicate any significant interactions. The standard Gibb's free energy for DNA binding was calculated from the following relation[4] $\Delta G^{\circ}_b = -RT \ln K_b$ and was found to be -31.588 KJ M^{-1}.

1. S., A. Chakraborty, S. P. Dash, A. K. Panda, R. Acharyya, A. Biswas, S. Mukhopadhyay, S. K. Bhutia, A. Crochet, Y. P. Patil, M. Nethaji and R. Dinda, *Dalton Trans*., 2015, **44**, 6140–6157.
2. D. Sarkar, P. Das, S. Basak and N. Chattopadhyay, *J. Phys. Chem. B*, 2008, **112**, 9243–9249.
3. (a) R.P. Paitandi, R.K. Gupta, R.S. Singh, G. Sharma, B. Koch and D.S. Pandey, *Eur. J. Med. Chem*., 2014, **84**, 17–29; (b) R.K. Gupta, G. Sharma, R. Pandey, A. Kumar, B. Koch, P.Z. Li, Q. Xu and D.S. Pandey, *Inorg. Chem*., 2013, **52**, 13984–13996.
4. L. H. Abdel-Rahman, R. M. El-Khatib, L. A.E. Nassr, A. M. Abu-Dief and F. El-Din Lashin, *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.*, 2013, **111**, 266–276.



UV-Vis spectra of complex **2**(L_{Et}) **(**6.67 x 10^{-5} M, 30 mM Tris–HCl, pH 7.4） after addition of CT-DNA (0-7 μM) at 298 K. The arrow shows the direction of change in absorbance. Inset: Plot of [DNA]/(ε_a-ε_f) vs [DNA].

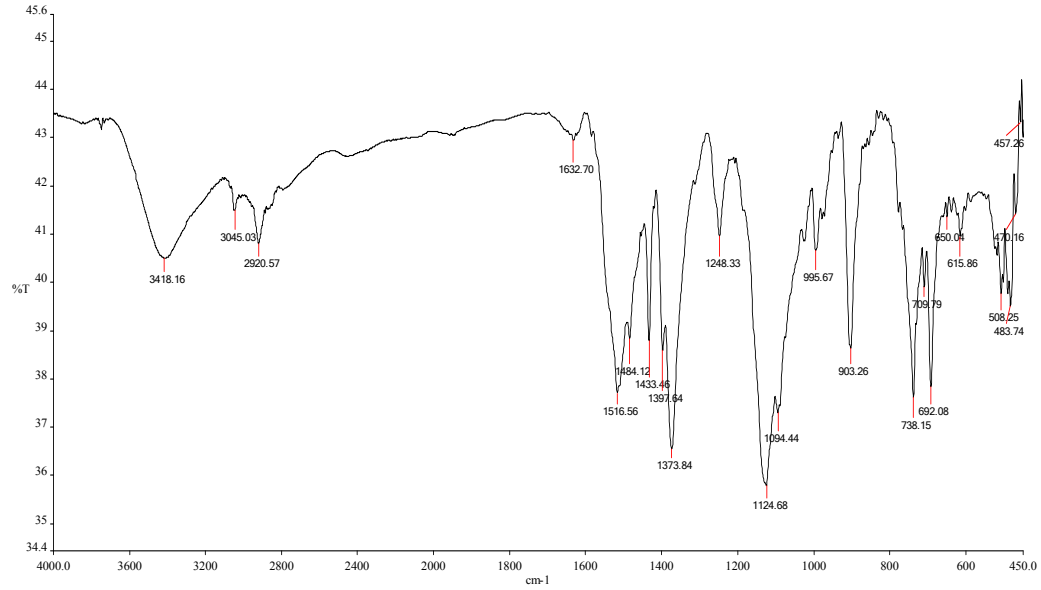


Fig. S1: IR spectrum of **2**(L_{Me})

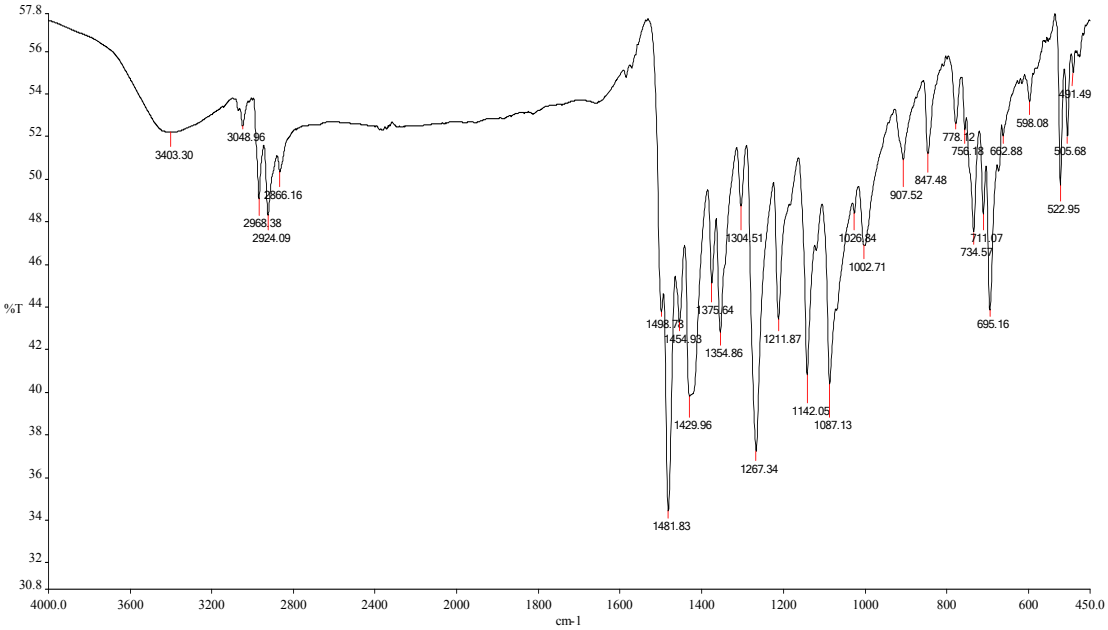


Fig. S2: IR spectrum of **2**(L_{Et})

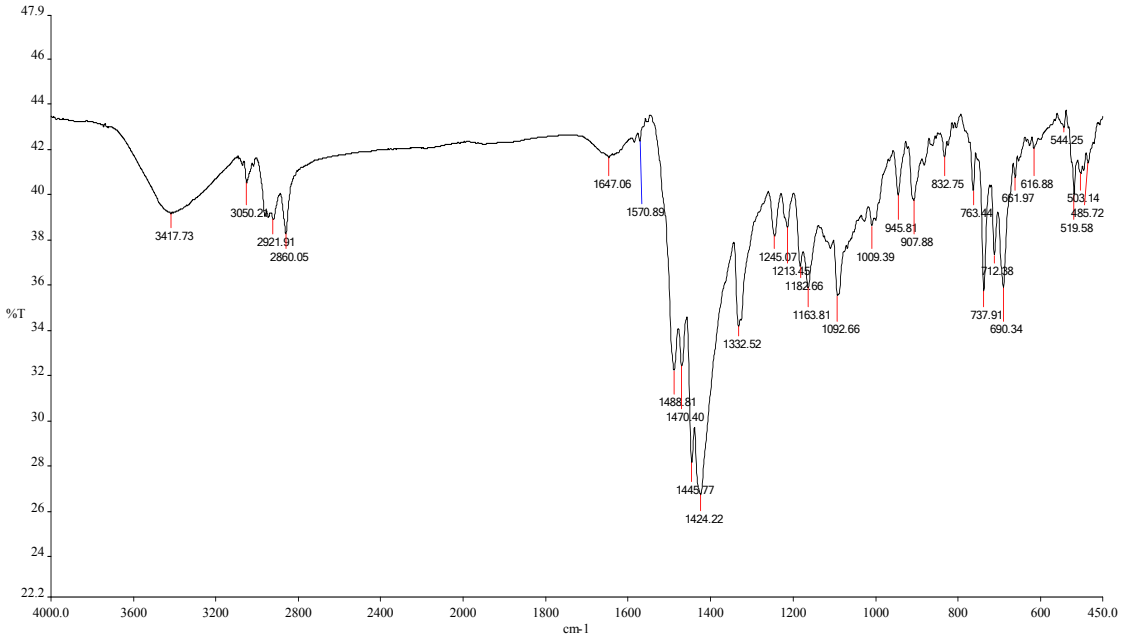


Fig. S3: IR spectrum of **2**(L_{Pyr})

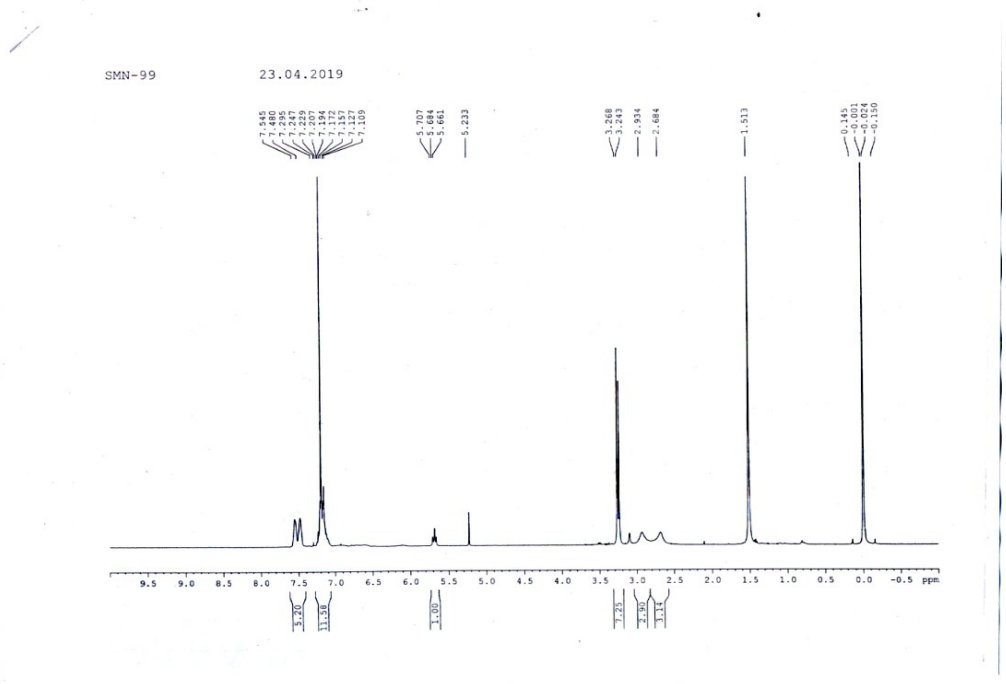


Fig. S4: ^{1}H NMR spectrum of **2**(L_{Me})

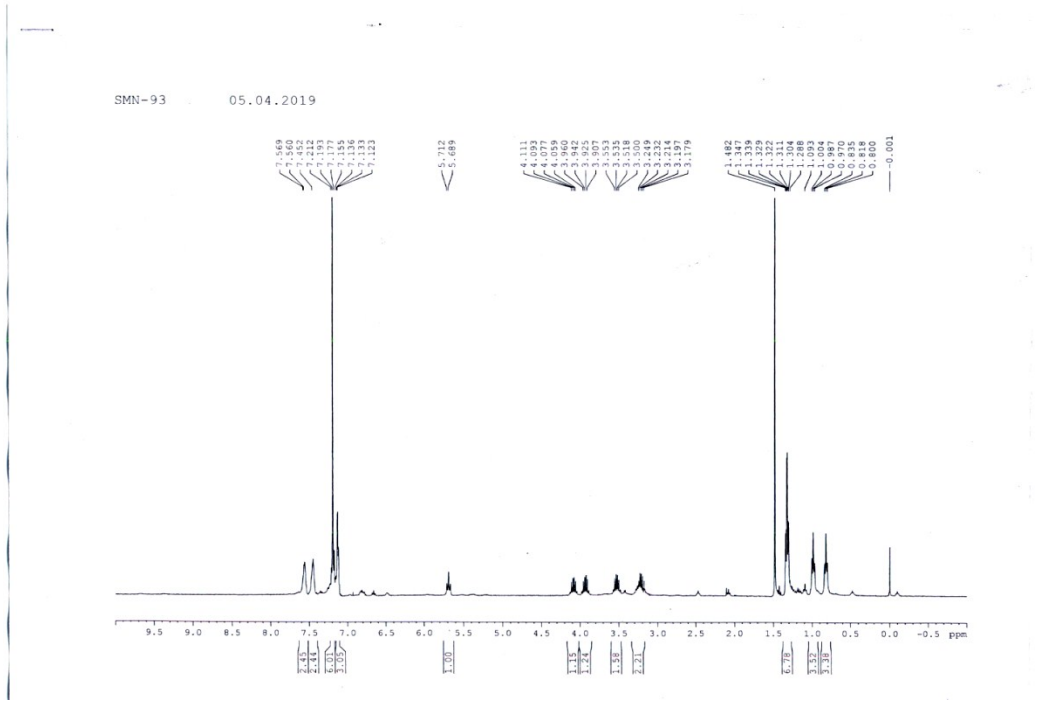


Fig. S5: ^{1}H NMR spectrum of **2**(L_{Et})

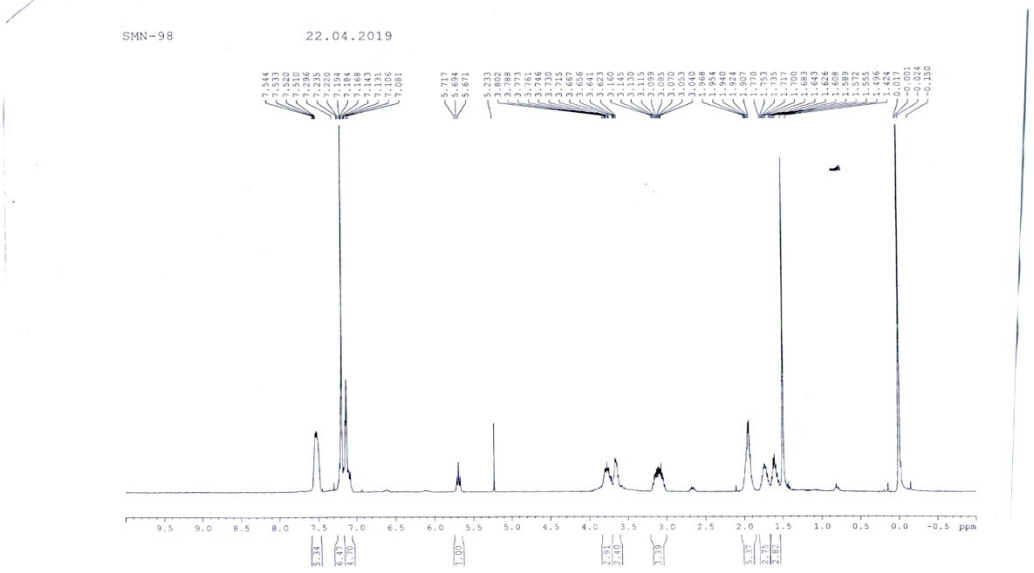


Fig. S6: ^{1}H NMR spectrum of **2**(L_{Pyr})

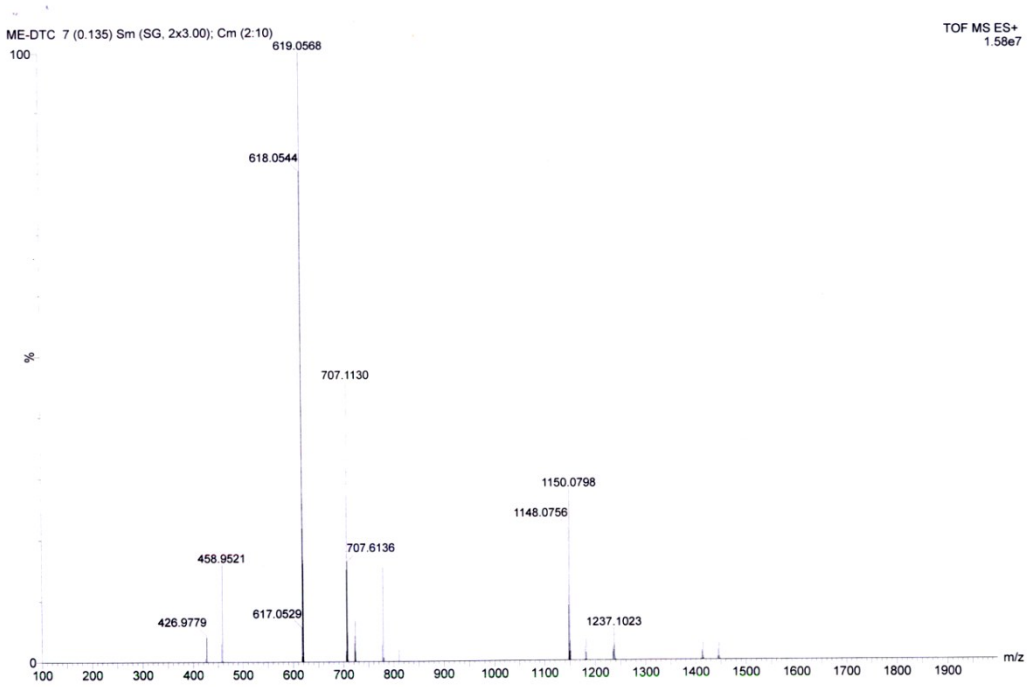


Fig. S7: ESI Mass spectrum of **2**(L_{Me})

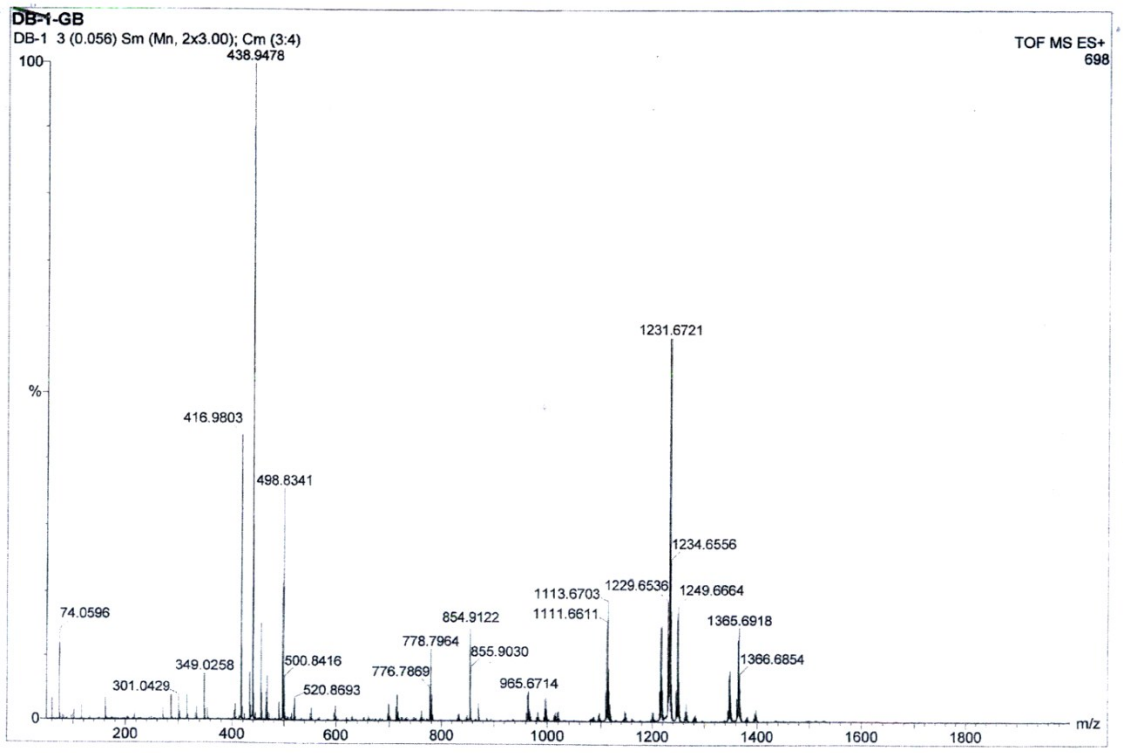


Fig. S8: ESI Mass spectrum of **2**(L_{Et})

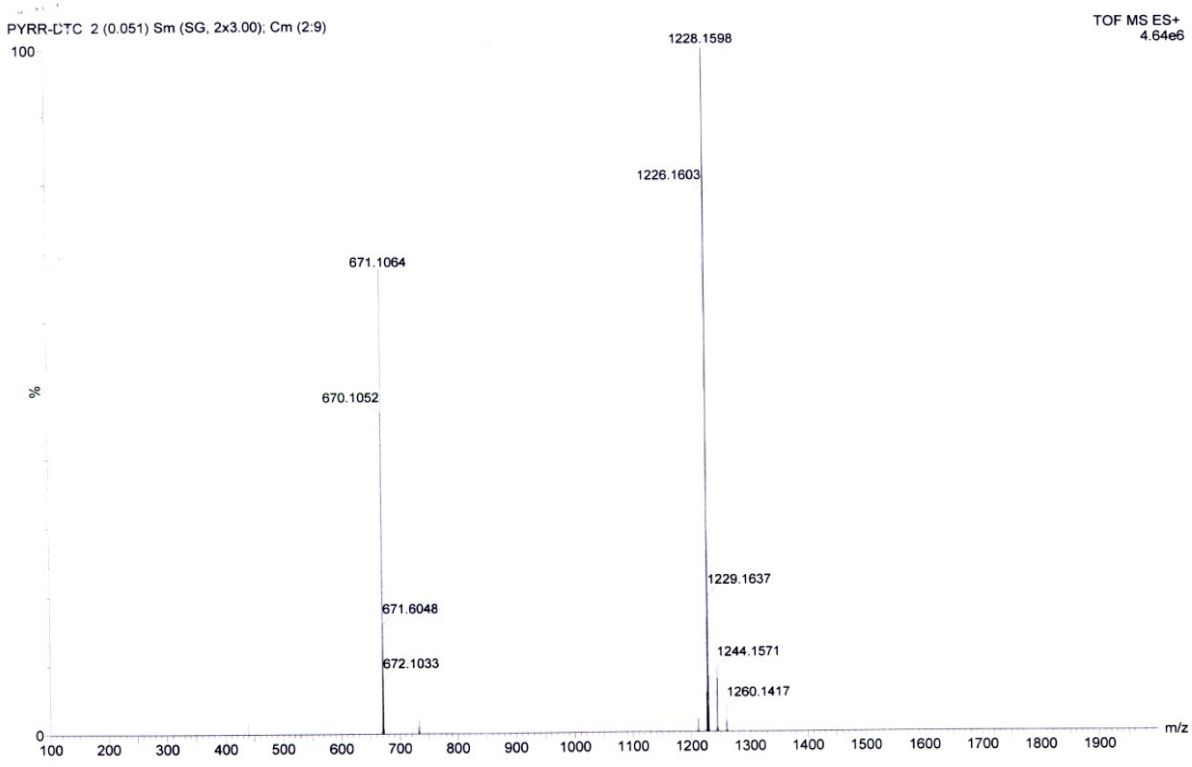

PYRR-DTC 2 (0.051) Sm (SG, 2x3.00); Cm (2:9)
TOF MS ES+
4.64e6
100
%
0
1228.1598
1226.1603
671.1064
670.1052
1229.1637
671.6048
1244.1571
672.1033
1260.1417
m/z
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900

Fig. S9: ESI Mass spectrum of **2**(L_{Pyr})

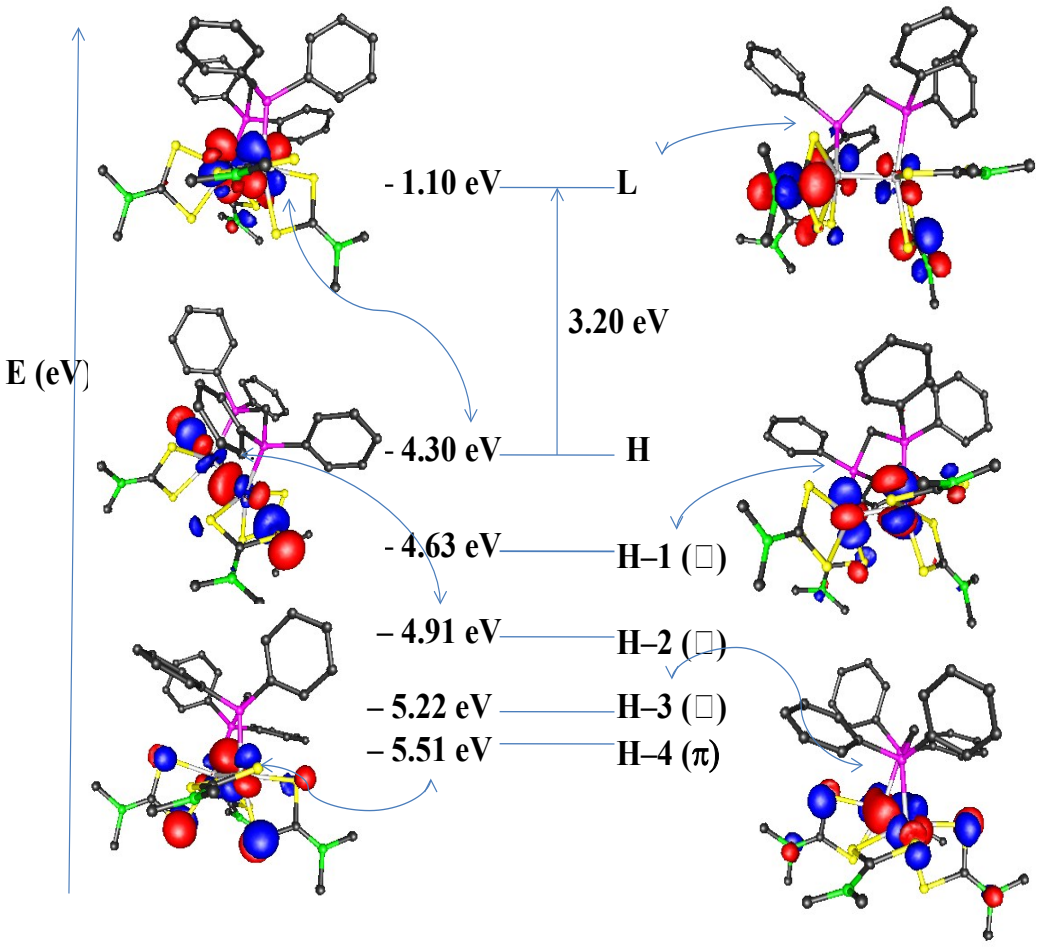


Fig. 10: Illustration of the 0.04 contour surface diagrams of five highest occupied and one lowest unoccupied MOs calculated by DFT for **2**(L_{Me}).

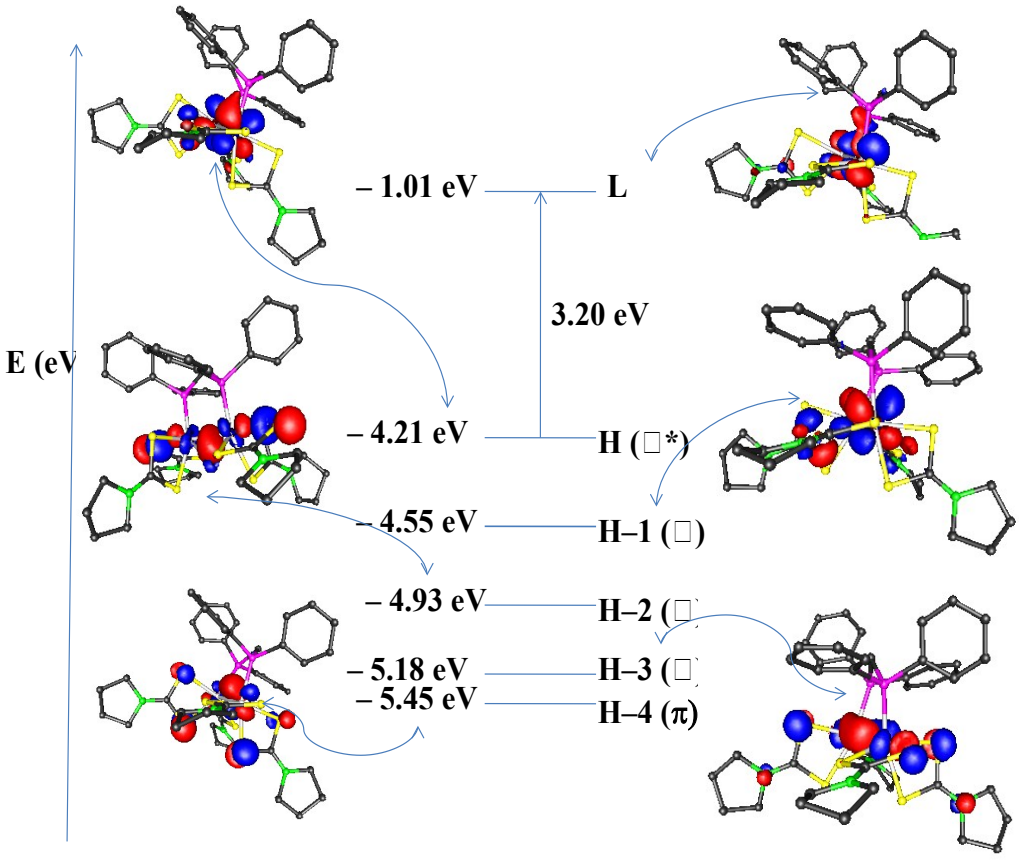


Fig. 11: Illustration of the 0.04 contour surface diagrams of five highest occupied and one lowest unoccupied MOs calculated by DFT for **2**(L_{Pyr}).

Tables

Table S1. Frontier molecular orbital compositions (%) in the ground state for **2**(L_{Me}).

Orbital	Energy	Contribution (%)

	(eV)	Re	L_{Me}	dppm
H – 5	– 5.6332	11.2	85.5	3.3
H – 4	– 5.5127	35.1	59.8	5.1
H – 3	– 5.2265	42.8	56	1.2
H – 2	– 4.9719	35.5	64.1	0.4
H – 1	– 4.6343	51.9	39.4	8.7
H	– 4.3038	58.7	32.9	8.4
L	– 1.1037	31.1	61.7	7.2
L + 1	– 1.0781	45.6	37.7	16.7
L + 2	– 0.8725	18.6	26	55.4
L + 3	– 0.8207	8.6	50.3	41.1
L + 4	– 0.7337	11.4	39.4	49.2
L + 5	– 0.5688	18.6	31.9	49.5

Table S2. Frontier molecular orbital compositions (%) in the ground state for **2**(L_{Et}).

Orbital	Energy (eV)	Contribution (%)		
		Re	L_{Et}	dppm
H – 5	– 5.5049	14.1	83	2.9
H – 4	– 5.3702	31.5	63	5.3
H – 3	– 5.1950	42.7	55.9	1.4
H – 2	– 4.8529	36.3	63	0.7
H – 1	– 4.5110	51.2	40.3	8.5
H	–4.1728	58.1	33.4	8.5
L	– 0.9853	27.3	61.8	10.9
L + 1	– 0.9694	50.6	31.2	18.2
L + 2	– 0.8051	15.5	20.9	63.6
L + 3	– 0.7384	10.9	33.2	55.9
L + 4	– 0.6451	8.4	63.9	27.7
L + 5	– 0.4968	2.8	55.3	41.9

L + 7	– 0.4154	2.8	60.3	36.9
L + 9	– 0.3863	5.6	38.8	55.6

Table S3. Frontier molecular orbital compositions (%) in the ground state for **2**(L_{Pyr}).

Orbital	Energy (eV)	Contribution (%)		
		Re	L_{Pyr}	dppm
H – 5	– 5.5775	12.6	84.2	3.2
H – 4	– 5.4509	32.3	62.2	5.5
H – 3	– 5.1824	42.5	56.1	1.4
H – 2	– 4.9303	35.1	64.0	0.6
H – 1	– 4.5579	51.0	40.8	8.2
H	– 4.2167	58.7	33.0	8.3
L	– 1.0155	57.1	21.4	21.5
L + 1	– 0.9973	23.6	71.4	5.0
L + 2	– 0.8275	15.4	16.4	68.2
L + 3	– 0.7476	10.0	27.8	62.2
L + 4	– 0.6517	9.6	66.4	24.0
L + 5	– 0.5085	8.5	15.2	76.3

Table S4: Mulliken Atomic Charges for **2**(L_{Me}).

Atoms	Charges
Re	0.078655
Re	0.031476
S	-0.212053
S	-0.388662
S	-0.244797
S	-0.238092
S	-0.180303
S	-0.174456

S	-0.245493
S	-0.380286
P	0.276835
P	0.358948

Table S5: Mulliken Atomic Charges for **2**(L_{Et}).

Atoms	Charges
Re	0.087473
Re	0.035147
S	-0.190583
S	-0.394446
S	-0.249968
S	-0.239337
S	-0.164246
S	-0.171701
S	-0.233487
S	-0.386045
P	0.267346
P	0.345154

Table S6: Mulliken Atomic Charges for **2**(L_{Pyr}).

Atoms	Charges
Re	0.099371
Re	0.013963
S	-0.199145
S	-0.397337
S	-0.242086
S	-0.243805
S	-0.180533
S	-0.181422
S	-0.250833
S	-0.388515
P	0.277940
P	0.362673

Table S7: Cartesian coordinates (Å) for DFT energy-minimized model of **2**(L_{Me}).

Atoms	**x**	**y**	**z**
Re	-0.726750	-1.033008	-1.252098

Re	1.051474	-0.676619	0.180217
S	3.080444	-1.143536	-1.079701
S	2.502696	-0.023285	2.521565
S	-2.745781	-0.138165	-0.241501
S	1.765559	-2.974221	0.671257
S	0.441182	-2.706668	-2.616726
S	-0.316667	-0.698194	2.216458
S	-1.958676	-2.879595	-0.170091
P	-0.152502	0.881889	-2.538453
P	1.125022	1.714471	0.094592
S	-2.144514	-1.780836	-3.567916
C	-1.409644	1.728288	-3.624120
N	-4.417544	-2.090867	0.708362
N	0.816202	-0.335451	4.630325
C	5.324170	-3.283826	-1.302988
H	6.282056	-3.552835	-0.817494
H	5.344866	-2.215819	-1.578424
C	-0.990441	2.646355	-4.614574
H	0.081055	2.797475	-4.802077
C	3.984623	1.981834	0.136766
H	4.013268	0.904030	0.336700
C	-3.203410	-1.753528	0.210549
C	2.741715	2.627558	-0.024884
C	-2.793483	1.549189	-3.411869
H	-3.140377	0.841919	-2.646863

C	4.202490	-4.837435	0.275825
H	3.522209	-4.808118	1.144318
H	5.223085	-5.087066	0.623086
C	-1.745739	3.420127	2.580943
H	-2.843663	3.435348	2.626331
C	0.239421	2.324398	-1.433270
H	-0.741238	2.736729	-1.132803
H	0.785596	3.132737	-1.955216
C	1.271567	0.773860	-3.706999
C	-5.387946	-1.075253	1.107630
H	-6.406245	-1.412089	0.834259
H	-5.169101	-0.128463	0.585427
C	1.095441	-0.005239	-4.875715
H	0.118994	-0.470896	-5.070915
C	-3.307438	3.174318	-5.156927
H	-4.043567	3.730788	-5.753917
C	2.732611	4.017779	-0.294741
H	1.777501	4.551883	-0.395834
C	2.528668	1.369531	-3.471351
H	2.703558	1.971501	-2.570607
C	1.863422	0.139077	5.528584
H	1.818624	-0.429288	6.477190
H	2.848171	-0.015804	5.055283
C	-0.986043	4.083087	3.561103
H	-1.485099	4.631155	4.372712

C	5.167305	4.080031	-0.255041
H	6.107680	4.641489	-0.345738
C	5.188072	2.702777	0.022559
H	6.145646	2.179827	0.152607
H	-5.352809	-0.895734	2.203119
H	3.856957	-5.630089	-0.421232
H	5.209995	-3.887546	-2.228125
H	-2.078815	-5.038934	-5.926682
C	-4.719152	-3.468678	1.089229
H	-4.113426	-4.161480	0.479806
H	-5.792319	-3.668307	0.909149
C	3.933006	4.737551	-0.412614
H	3.903092	5.815766	-0.623338
C	3.583952	1.201657	-4.387783
H	4.554214	1.676489	-4.186327
C	-1.840976	-3.977613	-5.719206
H	-1.486567	-3.501622	-6.659668
H	-2.754749	-3.455513	-5.387278
C	-3.734207	2.266465	-4.172021
H	-4.807142	2.106349	-3.996146
C	3.396334	0.437142	-5.551325
H	4.218871	0.311232	-6.269396
C	0.990642	-0.342378	3.274948
C	2.147121	-0.165672	-5.791728
H	1.990009	-0.764171	-6.700233

C	-1.931055	3.362608	-5.375010
H	-1.584455	4.068542	-6.143003
C	0.418153	4.034739	3.496558
H	1.024151	4.542884	4.260079
H	1.166417	-4.231925	-5.343557
H	-1.126859	0.423083	5.096026
H	-4.494908	-3.649544	2.161749
C	-0.519530	-0.502034	5.196079
H	-1.049046	-1.320802	4.674761
H	-0.426550	-0.758606	6.266891
H	1.748406	1.222094	5.751953
N	-0.835523	-3.900789	-4.665312
C	-0.854981	-2.903246	-3.728332
C	3.162608	-2.690135	-0.298930
N	4.223110	-3.530543	-0.375778
C	0.342256	-4.750797	-4.807612
H	0.063811	-5.659222	-5.372107
H	0.714851	-5.046058	-3.809248
C	-1.105814	2.726274	1.539461
H	-1.720704	2.185945	0.806771
C	1.057303	3.344268	2.451245
H	2.153251	3.310445	2.418139
C	0.303451	2.697557	1.446232

Table S8: Cartesian coordinates (Å) for DFT energy-minimized model of **2**(L_{Et}).

Atoms	x	y	z
Re	8.331601	6.794465	5.088970
Re	10.128647	7.161095	6.496471
S	12.144224	6.700746	5.214419
S	11.611391	7.815339	8.816941
S	6.322555	7.676040	6.126732
S	10.854326	4.866089	6.981205
S	9.486302	5.124914	3.699834
S	8.795068	7.118942	8.558178
S	7.129905	4.939924	6.188622
P	8.878019	8.705454	3.786318
P	10.193535	9.551285	6.397943
S	6.871088	6.029363	2.809750
C	7.600346	9.546657	2.720426
N	4.672972	5.713225	7.094011
N	10.008781	7.358469	10.960851
C	14.455279	4.669318	5.052976
H	15.348153	4.181621	5.489910
H	14.607734	5.763886	5.125376
C	8.000312	10.466125	1.723190
H	9.068115	10.621413	1.518815
C	13.052945	9.825046	6.416608
H	13.084730	8.750093	6.630323
C	5.879355	6.057120	6.587068

C	11.807768	10.466368	6.254407
C	6.220828	9.362456	2.954651
H	5.889387	8.654683	3.725947
C	13.327505	3.056284	6.663111
H	12.799928	3.231849	7.620598
H	14.385245	2.834410	6.905128
C	7.338989	11.276125	8.887368
H	6.241550	11.280999	8.945531
C	9.290260	10.153337	4.876501
H	8.316087	10.573098	5.187355
H	9.833380	10.954668	4.340878
C	10.279755	8.595877	2.590198
C	3.662302	6.745052	7.385723
H	2.669396	6.270958	7.260660
H	3.755219	7.524701	6.605085
C	10.081013	7.822234	1.421628
H	9.100573	7.358962	1.241389
C	5.673061	10.984790	1.217252
H	4.925477	11.538177	0.631716
C	11.795331	11.853002	5.966273
H	10.838995	12.384760	5.864640
C	11.542972	9.186090	2.806413
H	11.735367	9.783148	3.706920
C	11.168652	7.586931	11.835867
H	11.055683	6.912894	12.708751

H	12.066988	7.262625	11.276928
C	8.102596	11.978005	9.837134
H	7.606907	12.543475	10.638645
C	14.230146	11.919387	5.989128
H	15.169068	12.480921	5.884809
C	14.254592	10.546051	6.284997
H	15.213757	10.026163	6.415765
C	3.788279	7.382788	8.776771
H	3.627273	6.646537	9.586380
H	3.031060	8.183434	8.891137
H	4.788595	7.835047	8.910421
C	4.369083	4.302865	7.396991
H	4.850367	3.689702	6.610384
H	3.273878	4.177995	7.291144
C	12.993801	12.572894	5.830972
H	12.960837	13.648177	5.606131
C	12.581432	9.019904	1.870631
H	13.556554	9.490763	2.057321
C	7.036156	3.767841	0.736647
H	7.453171	3.428710	-0.233108
H	6.583858	4.763498	0.572479
C	5.265450	10.075840	2.209186
H	4.196016	9.912026	2.402244
C	12.370820	8.262168	0.706572
H	13.179610	8.138380	-0.027297

C	10.127411	7.438672	9.602624
C	11.115641	7.663722	0.485708
H	10.939364	7.072232	-0.423798
C	7.045102	11.178396	0.977381
H	7.376709	11.885502	0.203872
C	9.505989	11.944688	9.756041
H	10.114752	12.481662	10.497168
C	5.974218	2.783666	1.246506
H	6.400194	1.777693	1.430068
H	5.161583	2.676442	0.500906
H	5.531796	3.152680	2.190490
C	7.788553	8.246008	11.794568
H	8.215465	8.969742	12.513734
H	6.812131	7.905174	12.193096
H	7.605416	8.774529	10.840624
C	8.713090	7.037988	11.579389
H	8.211297	6.293974	10.928929
H	8.928214	6.537807	12.544050
C	4.838416	3.834533	8.782043
H	5.929502	3.976069	8.893623
H	4.619277	2.755622	8.905252
H	4.328889	4.379621	9.598639
C	12.681504	1.878254	5.919503
H	11.632286	2.110022	5.657693
H	12.682009	0.980513	6.568632

H	13.226879	1.625353	4.990854
C	11.347815	9.040193	12.298047
H	11.437126	9.713953	11.425913
H	12.273313	9.131549	12.900925
H	10.501836	9.386787	12.921143
N	8.163267	3.934559	1.665572
C	8.166608	4.917134	2.613352
C	12.243977	5.155036	5.998201
C	14.280957	4.266266	3.581666
H	14.191115	3.170424	3.460983
H	15.159396	4.602432	2.996261
H	13.381353	4.742323	3.149422
N	13.312594	4.328486	5.919673
C	9.275981	2.983250	1.544324
H	8.847841	2.009509	1.232381
H	9.710138	2.838629	2.552170
C	10.360522	3.436955	0.556631
H	9.950821	3.574287	-0.463379
H	11.166766	2.679158	0.497173
H	10.808942	4.393578	0.884081
C	7.974441	10.559857	7.858287
H	7.358099	9.991669	7.148123
C	10.140716	11.231453	8.723348
H	11.236612	11.212488	8.675417
C	9.382871	10.547035	7.747099

Table S9: Cartesian coordinates (Å) for DFT energy-minimized model of **2**(L_{Pyr}).

Atoms	x	y	z
Re	-0.565715	-0.429914	-1.188432
Re	1.210528	-0.034358	0.227504
S	3.243736	-0.508326	-1.033689
S	2.698811	0.687305	2.561170
S	-2.593694	0.462561	-0.180700
S	1.942845	-2.323207	0.766778
S	0.601496	-2.120472	-2.540381
S	-0.131212	-0.041095	2.285128
S	-1.772789	-2.282486	-0.071265
P	-0.018599	1.464706	-2.510086
P	1.269233	2.352492	0.099821
S	-2.025022	-1.242902	-3.484230
C	-1.287587	2.283296	-3.604006
N	-4.197089	-1.484028	0.842328
N	1.009252	0.488146	4.648698
C	5.529779	-2.637200	-1.196669
C	6.263208	-3.989943	-1.196252
H	6.147449	-1.823516	-0.760230
C	-0.880527	3.184557	-4.614737
H	0.188802	3.338144	-4.812344
C	4.126894	2.646552	0.108310

H	4.166639	1.572999	0.328058
C	-3.011373	-1.150368	0.307645
C	2.876663	3.278465	-0.051239
C	-2.668833	2.100551	-3.378766
H	-3.005564	1.405293	-2.598426
C	4.454120	-4.162040	0.398975
H	4.179641	-4.007728	1.459889
C	5.918482	-4.583180	0.185416
C	-1.598408	4.070584	2.580140
H	-2.695900	4.067792	2.638190
C	0.366208	2.929274	-1.431415
H	-0.616420	3.336245	-1.130089
H	0.900478	3.734673	-1.970037
C	1.400022	1.348733	-3.685120
C	-5.281798	-0.521525	1.112550
C	-6.499116	-1.425265	1.373046
H	-5.404134	0.161940	0.250944
C	1.225993	0.541540	-4.834866
H	0.253779	0.060949	-5.014065
C	-3.204168	3.689195	-5.150946
H	-3.947558	4.230099	-5.753318
C	2.852739	4.663282	-0.346691
H	1.891917	5.187174	-0.447273
C	2.652403	1.961717	-3.469662
H	2.825905	2.584712	-2.583110

C	2.087913	0.823071	5.593092
H	2.359573	1.896234	5.494923
H	2.995189	0.234349	5.359503
C	-0.839167	4.772089	3.533532
H	-1.338451	5.332728	4.336477
C	5.287079	4.747160	-0.335447
H	6.221524	5.314793	-0.447146
C	5.322645	3.375397	-0.033043
H	6.286081	2.862806	0.095271
H	-5.024207	0.098556	1.997553
H	-0.682958	0.289762	7.493171
C	-4.563575	-2.866691	1.206588
H	-4.699904	-3.469757	0.284016
C	-5.874858	-2.692369	1.993068
C	4.045447	5.391112	-0.491055
H	4.003764	6.464997	-0.721243
C	3.704781	1.783513	-4.387467
H	4.671532	2.271577	-4.201279
C	-1.750597	-3.525715	-5.561551
C	-1.129403	-4.530162	-6.548058
H	-2.055040	-2.569235	-6.026986
C	-3.618812	2.798143	-4.145671
H	-4.689636	2.635737	-3.959007
C	3.518880	0.991106	-5.532531
H	4.339250	0.856614	-6.251631

C	1.180965	0.393479	3.309073
C	2.274465	0.370794	-5.752642
H	2.118728	-0.250445	-6.646024
C	-1.830438	3.880716	-5.382381
H	-1.493174	4.573737	-6.166177
C	0.564809	4.746039	3.453491
H	1.170698	5.283768	4.196657
H	-2.647140	-3.937578	-5.049310
C	1.468506	0.504326	6.964916
H	-1.078317	0.855328	4.785220
H	-3.749312	-3.334946	1.791555
H	-0.226815	1.878284	6.813560
H	-6.527997	-3.581276	1.920425
H	1.915552	1.105074	7.778686
H	1.624586	-0.564826	7.213630
C	-0.287518	0.291356	5.317381
H	-0.570850	-0.783466	5.287482
C	-0.032196	0.788831	6.751218
H	0.637294	-5.850634	-6.250099
H	-5.655786	-2.525508	3.066799
H	-6.999773	-1.672913	0.415669
H	-7.248457	-0.942452	2.026960
H	3.738713	-4.897073	-0.027353
H	5.203226	-2.304345	-2.200030
H	1.327842	-3.774021	-5.134988

H	5.864993	-4.638016	-2.002585
H	-0.698103	-6.104280	-5.091113
H	-1.891316	-5.160699	-7.042835
H	-0.576084	-3.990131	-7.342808
N	-0.672236	-3.298559	-4.584495
C	-0.704223	-2.325711	-3.639939
C	3.316608	-2.043663	-0.235142
H	7.350130	-3.878121	-1.364487
H	6.051826	-5.679513	0.235330
H	6.561407	-4.132278	0.967725
N	4.356791	-2.887037	-0.336977
C	0.425156	-4.270684	-4.716515
C	-0.149332	-5.333814	-5.669413
H	0.702953	-4.666781	-3.719945
C	-0.958494	3.361172	1.549119
H	-1.571780	2.790359	0.838480
C	1.203845	4.040009	2.418512
H	2.299784	4.023621	2.373343
C	0.449898	3.355436	1.439003

Table S10: Summary of X-ray crystallography for **2**(L_{Et})

Empirical formula	$C_{45}H_{62}N_4P_2Re_2S_8$

Formula weight	1349.80
Crystal system	Triclinic
Space group	P-1
a/Å	10.972(3)
b/Å	11.579(3)
c/Å	22.431(6)
α/°	85.129(7)
β/°	78.968(7)
γ/°	68.600(6)
Volume/Å^3	2603.9(11)
Z	2
μ/mm^{-1}	5.063
Reflections collected	28348
Independent reflections	11126
Goodness-of-fit on F^2	0.876
Final R indexes [I>=2σ (I)]	R_1 = 0.0594, wR_2 = 0.0872